Design and synthesis of π-conjugated molecules

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Design and synthesis of π-conjugated molecules

Toward systems with extended conjugation in one- and two-dimensions and n-doped materials

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Promotores: Prof. Dr. E. W. Meijer
Prof. Dr. R. M. Kellogg

Voorwoord

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Contents

Chapter 1

1.1 Introduction. 1
1.2 Synthesis of π-conjugated polymers 3
1.2.1.Polythiophene 3
1.2.1.1 Organometallic coupling 6
1.2.1.2 Electrochemical synthesis 8
1.2.1.3 Oxidative coupling 10
1.2.2. Polypyrrole 11
1.2.3. Polyaniline 13
1.2.4. Other heterocyclic polymers 15
1.2.4.1 Small Band Gab Polymers 16
1.2.4.2 Fused Monomers 17
1.2.4.3 Other Homopolymers 18
1.2.5. Poly(paraphenylene) 18
1.2.5.1 Oxidative coupling 18
1.2.5.2 Organometallic coupling 19
1.2.5.3 Dehydrogenation of polycyclohexylenes 20
1.2.6. Polyacetylene 21
1.2.6.1 Shirakawa route 21
1.2.6.2 The Luttinger route 22
1.2.6.3 Precursor route 22
1.2.6.4 Soluble polyacetylenes 23
1.2.7 Polydiacetylenes 24
1.2.8 Two-dimensional ladder structures 26
1.2.9. Phenylene-heteroarene copolymers 27
1.2.9.1 Direct polymerization 28
1.2.9.2 Precursor route 29
1.2.9.3 Oligomer polymerization 30
1.2.10. Poly(arylene vinylene)s 31
1.3 Synthesis of well-defined oligomers 33
1.3.1 Thiophene oligomers 33
1.3.2 Other oligomers 36
1.4 Aims of this thesis and survey of its contents 37

Chapter 2 Design and synthesis of regioregular poly(dodecyl-[2,2']-bithienyl

2.1 Introduction 39
2.2 Synthesis of regiorandom poly(3-dodecyl-[2,2']-bithienyl) 42
2.2.1 Monomer synthesis 42
2.2.2 Polymerization 43

2.3 Synthesis of regioregular poly(4-dodecyl-[2,2']-bithienyl) 44
2.3.1 Monomer synthesis 44
2.3.1.1 First approach 45
2.3.1.2 Second approach 46
2.3.2 Polymerization 48
2.4 Absorption spectroscopy and thermochromism 49
2.5 Discussion 51
2.6 Concluding remarks 54
2.7 Experimental section 54

Chapter 3 Synthesis of well-defined oligomers and polymers containing thiophene, phenylene and pyrrole moieties using the Stetter reaction

3.1 Introduction 61
3.1.1 The mechanisme of the Stetter reaction 62
3.2 Oligomers 66
3.2.1 Synthesis 66
3.2.2 Absorption spectroscopy 74
3.2.3 Discussion 75
3.3 Polymers 77
3.3.1 AA-BB-Polymerization 77
3.3.2 Characterization 83
3.3.3 AB-Polymerization 85
3.3.4 Discussion 87
3.4 Concluding remarks 89
3.5 Experimental section 89

Chapter 4 Design and synthesis of two-dimensional co-planar conjugated systems based on the pyrazine moiety

4.1 Introduction 107
4.2 Synthesis of one-dimensional systems 110
4.2.1 Model compounds 110
4.3 Synthesis of two-dimensional systems 112
4.3.1 Model compounds 113
4.3.2 Oligomers 114
4.3.3 Polymers 115
4.4 Characterization 116
4.4.1 Absorption spectroscopy 118
4.4.2 X-ray analysis of compound 4.27 120
4.5 Discussion 122
4.6 Concluding remarks 124
4.7 Experimental section 124

Chapter 5 Toward a stable n-doped conducting polymer

5.1 Introduction 129
5.2 Synthesis of 1,3-diketones 132
5.3 Copper complex formation 135
5.3.1 Keto-esters on both sides 135
5.3.2 Mixed complexes 136
5.4 Characterization 137
5.5 Discussion 138
5.6 Concluding remarks 139
5.7 Experimental section 140

Samenvatting 145

Chapter one

1.1 Introduction

Conjugated polymers are expected to become prime constituents in electronics based on organic materials. There are already some established applications and a considerable volume of precommercialization work is in progress. These bright prospects have led to an explosive growth in research effort on these materials during the last decade, both scientific[1] and industrial. This interest is due to substantial π-electron delocalization along their π-conjugated backbones, which gives rise to fascinating optical and non-linear optical properties and allows them to become good electrical conductors, typically when oxidized or reduced. The oxidation and reduction are usually referred to as doping. These properties may lead to materials with a variety of practical applications[2,3], such as optical signal processing and information storage, substitute materials for batteries and devices for solar energy conversion. Electroluminescence based devices also provide a rapidly expanding field of interest[4]. Furthermore, sloppy electronics using conjugated polymers as semiconductors in field-effect transistors (FET) and Scottky barrier diodes etcetera are feasible as a result of improved performances of these organic materials. However, the development of these possible applications has been limited by the low stability toward ambient conditions and lack of processability often characteristic of polyconjugated materials. Consequently, considerable efforts have been directed toward the preparation of molecules with improved processability and stability, and this activity has provided materials with significantly enhanced properties.

Several classes of polyconjugated molecules, either of high molecular weight (polymers), or of relatively low molecular weight (oligomers), have been synthesized, studied and applied. Polythiophenes, polypyrroles and other polymers with hetero atoms in the polymer main chain, such as polyaniline, are among the most important classes of heterocyclic polymers with extended π-conjugation. Polyaniline, although formally not a poly-heterocyclic, is included in this group since its properties are directly related to the presence of the nitrogen atoms. Another important class of conjugated materials consists of

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1 *Handbook of Conducting Polymers* Skotheim, T. A. Ed., Marcek Dekker Inc, New York, Basel **1986.**

2 Roth, S.; Graupner, W. *Synth. Met.* **1993**, *55-57*, 3623.

3 Wöhrle, D.; Meissner, D. *Adv. Mater.* **1991**, *3*, 129.

4 a) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; MacKay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1991**, *347*, 539. b) Braun, D.; Heeger, A. J. *Appl. Phys. Lett.* **1991**, *58*, 1982.

the hydrocarbon polymers, such as polyacetylenes, polyphenylenes and the alternating copolymer of phenylene and acetylenes; the poly(phenylene vinylene)s. The general insolubility and intractability of these polymers have, in the past, created problems both for the chemist, with respect to a detailed characterization, and for the potential users. Processability of polyacetylenes, polyphenylenes and poly(phenylene vinylene)s has been accomplished by using soluble precursor polymers, and the introduction of solubilizing side chains is an alternative successful strategy for overcoming processing difficulties of, for example, polythiophenes. In the case of poly(phenylene vinylene)s the attachment of side chains not only significantly enhances the solubility, but also modifies their electronic properties.

To obtain materials with excellent properties, high π-electron mobility is required, both intramolecular and intermolecular. Intramolecular mobility depends on the effective conjugation length. The through conjugation is interrupted by mis-couplings between adjacent rings such as the meta coupling in benzene or the α-ß coupling in thiophene (figure 1.1.a) and by steric repulsions of groups attached to the rings forcing the rings to adopt a non-planar conformation (figure 1.1.b). The intermolecular mobility, the transposition of

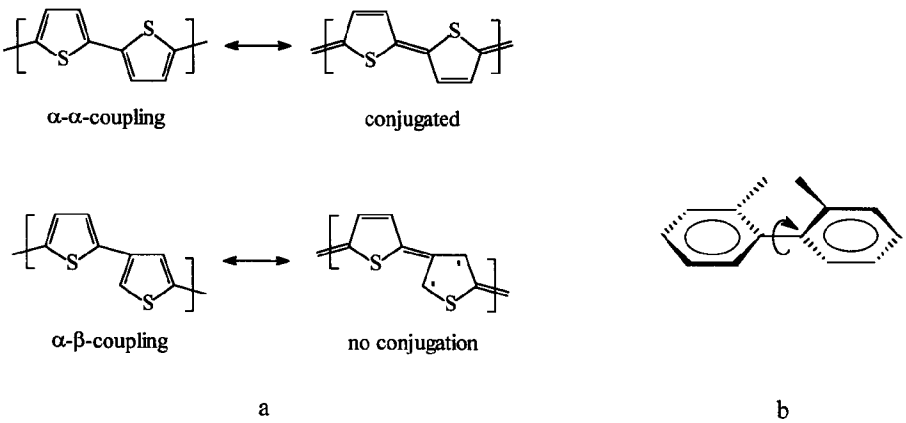


figure 1.1

charge carriers from one polymer chain to another, also called 'hopping', is necessary since these types of polymers are not of infinitive length. Hopping is facilitated by small interchain distances, which requires highly ordered and therefore crystalline materials. These preconditions clearly show the importance of well-defined and precise techniques for the synthesis of conjugated materials. Recent progress in the field of substituted polythiophenes has shown the significance of precision in the control over molecular structure in these aspects, i.e., defect free π-conjugation and regioregularity of the substituents. Alternatively, ordering can be accomplished by macroscopic modifications of

the materials, in order to align the polymer chains. A sixfold elongation of a poly(3-octyl thiophene) sample produces a 800-fold increase in conductivity[5].

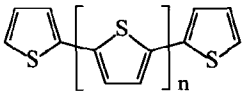
Considerable research efforts have been directed toward the synthesis of well-defined oligomers; the term well-defined is used to distinguish between low molecular weight polydisperse polymers with an average molecular weight and organic molecules with a distinct mass. Well-defined oligomers are mainly used as model compounds for the investigation of synthesis and properties of the corresponding polymers, but they can be used in certain applications as well.

In this chapter a comprehensive review of conjugated materials that have been presented in the literature is given. A detailed description of the physics and applications of these materials is beyond the scope of this thesis that will focus on the synthetic aspects of the field of π-conjugated polymers and well-defined oligomers.

1.2 Synthesis of π-conjugated polymers

1.2.1 Polythiophene

The first polythiophene synthesis has been described in 1883. Washing of benzene with sulfuric acid afforded after further treatment with sulfuric acid a black insoluble material[6]. Oligomerization of thiophene induced by phosphoric acid leads to the formation of the trimer[7]. It was not until the early 1980's, however, that any well-defined polymeric material was obtained. After the first syntheses by Yamamoto[8] and Lin[9], using the Grignard-type coupling of 2,5-dibromothiophene, a vast number of articles concerning synthesis and properties of polythiophenes has been published. Polythiophenes exhibit

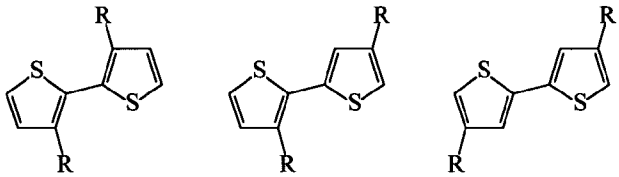


polythiophene

5 Ishikawa, H.; Amano, K.; Kobayashi, A.; Satoh, M.; Hasegawa, E. *Synth. Met.* **1994**, *64*, 49.
6 Meyer, V. *Chem. Ber.* **1883**, *16*, 1465.
7 Meisel, S. L.; Johnson, G. C.; Hartough, H. D. *J. Am. Chem. Soc.* **1950**, *72*, 1910, and references therein.
8 Yamamoto, T.; Sanechika, K.; Yamamoto, A. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 9.
9 Lin, J. W-P.; Dudek, L. P. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 2869.

favorable properties such as stability in both the neutral and the oxidized state under ambient conditions, but the numerous studies are also a result of the synthetic know-how for the preparation of (poly)thiophene and its derivatives[10].

The early problems concerning structural defects and solubility have attained much attention in the course of polythiophene research, and some elegant solutions have been found. Extended π-conjugation in polythiophenes is only possible in polymers with perfect 2,5-linked repeating units. Unfortunately, 2,4- and 2,3-couplings can be found as well. These undesired couplings are found when the polymers are prepared by (electro)oxidative polymerization methods. This is due to the fact that during the polymerization both the absolute oxidation potential of the α-position and the oxidation potential difference between the α- and ß-position decreases as the number of rings increases[11]. The occurrence of α,ß-linked thiophene rings interrupts the conjugation and as a result will give rise to inferior materials. Polythiophenes are, like other polyaromatic compounds, insoluble in organic solvents due to their rigid backbone This insolubility and related problems such as characterization and processability, have been overcome by the introduction of flexible side chains at one of the β-positions. Appropriate solubility is achieved by using thiophenes with one alkyl side chain consisting of more than three carbon units at every repeating unit[12]. However, in 3-substituted polythiophenes there are several coupling patterns possible; the head-to-head, the head-to-tail and the tail-to-tail isomers[13,14]. The



head-to-head head-to-tail tail-to-tail

head-to-head coupling is sterically unfavorable for coplanarity and causes considerable loss of conjugation, whereas the head-to-tail couplings display only a limited effect on the conjugation. These significant differences in coplanarity between head-to-head and head-to-tail couplings show the subtilities in the trade-off between resonance energy and steric hindrance in polyheterocycles. Studies of regioregular polythiophenes, recently made

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10 *Thiophene and its derivatives* vol. 1-6 Gronowitz, S. Ed., *Weisberger's The Chemistry of Heterocyclic Compounds*, Wiley Interscience.

11 Roncali, J.; Lemaire, M.; Garreau, R.; Garnier, F. *Synth. Met.* **1987**, *18*, 139.

12 Jen, K-W.; Miller, G. G.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1346.

13 Leclerc, M.; Diaz, F. M.; Wegner, G. *Makromol. Chem.* **1989**, *190*, 3105.

14 Sato, M.; Morii, H. *Macromolecules* **1991**, *24*, 1196.

accessible via a number of elegant routes, have shown that the crystallinity is increased with regioregularity and that the possibility of side-chains crystallinity is essential for optimal properties. For the case of regiorandom polymers the optimal chain length of the alkyl side-chains for properties like conductivity and optical non-linearities has been determined to be in the range of seven to nine carbon atoms[15]; the conductivity of doped regioregular polythiophene with a n-dodecyl side chain surpasses that of the n-octyl substituted polymer[16]. Even self-assembly in thin films is observed in the case of regioregular substituted polythiophenes. In addition to improved solubility, the introduction of side chains in the 3- and/or 4-position also decreases the rate of α,ß-couplings, since (one of) the ß-positions are already occupied[17,18]. The use of 3,4-disubstituted monomers, however, results in a significant loss of coplanarity of the thiophene rings for alkyl substituents, due to the presence of head-to-head couplings only[19]. In the case of one or two alkoxy-substituents, however, the presence of an oxygen atom attached to the thiophene ring leads to a decreased steric hindrance and the loss of conjugation is limited.

Besides conductivity, polythiophenes exhibit interesting optical properties including luminescence, thermochromism and solvatochromism. Photo- and electroluminesence depend on the effective conjugation length of the polythiophenes and, therefore, the color can be tuned by varying the number and positions of the alkyl side-chains[20], or the regioregularity in the materials[21]. Thermochromism[22,23,24] and solvatochromism[25] arise from the ability of alkyl substituted polythiophenes to adopt two different conformations depending on the temperature and solvent; a predominantly co-planar structure in an aggregated form at lower temperatures or in a non-solvent and a disordered non-planar form at higher temperatures or in a good solvent. The conformation-

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15 Roncali, J.; Garreau, R.; Yasser, A.; Marque, P.; Garnier, F.; Lemaire, M. *J. Phys. Chem.* **1987**, *91*, 6706.

16 McCullough, R. D.; Tristram-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, *115*, 4910.

17 Waltman, R. J.; Bargon, J.; Diaz, A. F. *J. Phys. Chem.* **1983**, *87*, 1458 .

18 Tourillon, G.; Garnier, F. *J. Phys. Chem.* **1983**, *87*, 2289.

19 Leclerc, M.; Daoust, G. *J. Chem. Soc., Chem. Commun.* **1990**, 273.

20 Gill, R. E.; Malliaras, G. G.; Wildeman, J.; Hadziioannou, G. *Adv. Mater.* **1994**, *6*, 132.

21 Xu, B.; Holdcroft, S. *Macromolecules* **1993**, *26*, 4457.

22 Salaneck, W. R.; Inganäs, O.; Thémans, B.; Nilsson, J. O.; Sjögren, B.; Österholm, J.-E.; Brèdas, J.-L.; Svensson, S.; *J. Chem. Phys.* **1988**, *89*, 4613.

23 Tashiro, K.; Ono. K.; Minagawa, Y.; Kobayashi, M.; Kawai, T.; Yoshino, K. *J. Polym. Sci., Part B: Polym. Phys.* **1991**, *29*, 1223.

24 Ekeblad, P. O.; Inganäs, O. *Polym. Commun.* **1991**, *32*, 436.

25 Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1071.

al changes are accompanied by large shifts in the absorption maxima, and also induce optical activity in chiral polythiophenes[26].

There is much controversy about the actual molecular weight of polythiophenes. GPC determinations relative to polystyrene standards overestimate the molecular weight by a factor of ten compared to the determination relative to oligothiophene standards[27]. A similar phenomenon was observed in the molecular weight determination of poly t-butylnaphthalene, although in this case the deviation is only ten per cent[28]. However, by a different technique, multi-angle light scattering (MALLS) molecular weight values were obtained two to five times larger than by GPC relative to polystyrene standards[29]

For the preparation of polythiophenes three main synthetic routes have been employed, namely: organometallic coupling, oxidative coupling and electrochemical synthesis. These will be discussed in sections 1.2.1.1 to 1.2.1.3 below.

1.2.1.1 Organometallic coupling

Nickel- and palladium-catalyzed cross-coupling of an organometallic compound with an organohalide is a well-known method for the coupling of heterocycles[30]. Organomagnesium derivatives are most widely employed in the polythiophene synthesis, despite the availability of a large number of organometallic species[31]. The reaction of dibromothiophene with magnesium and subsequent polymerization under the action of a nickel catalyst has been described in 1980, with a yield of 40 to 60% based on dibromothiophene[8,9]. The yields are improved up to 93% by the use of 2,5-diiodothiophene and Ni(dppp)Cl_2 as catalyst[32]. 3-Alkyl-substituted polythiophenes, with molecular weights varying from 2500 to 18000, have been synthesized by this method as well, although the structures obtained all are regiorandom[33,34]. This regiorandomness has been explained as arising from the inhomogeneity of the Grignard iodide mixture, consisting of the diiodo-, the bis-Grignard and two monoiodo-mono-Grignard com-

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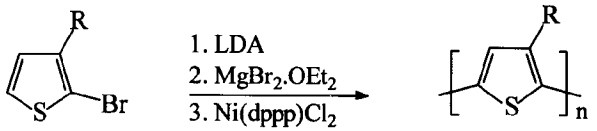
26 Bouman, M. M.; Meijer, E. W. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1994**, *35*, 309.
27 Havinga, E. E.; van Horssen, L. W. *Makromol. Chem., Macromol. Symp.* **1989**, *24*, 67.
28 Fahnenstich, U.; Koch, K.-H.; Müllen, K. *Makromol. Chem., Rapid Commun.* **1989**, *10*, 563.
29 Pomerantz, M.; Tseng, J. J.; Zhu, H.; Sproull, S. J.; Reynolds, J. R.; Uitz, R.; Arnott, H. J. *Synth. Met.* **1991**, *41-43*, 825.
30 Tamao, K; Kodama, S.; Nakajima, I.; Kumada, M.; Minato, A.; Suzuki, K. *Tetrahedron* **1982**, *39*, 3347.
31 Kalinin, V. N. *Synthesis* **1992**, 413.
32 Kobayashi, M.; Chen, J.; Chung, T.-C.; Moraes, F.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1984**, *9*, 77.
33 Elsenbaumer, R. L.; Yen, K. Y.; Oboodi, R. *Synth. Met.* **1986**, *15*, 169.
34 Inganäs, O.; Salaneck, W. R.; Österholm, J.-E.; Laakso, J. *Synth. Met.* **1988**, *22*, 395.

pounds[35,36]. The cross-coupling reaction has also been utilized for the monomer synthesis[37,38].

Regioregularity has been achieved by McCullough et al.[16,39,40], in the polymerization of 5-bromomagnesio-2-bromo-3-alkyl thiophenes as outlined in scheme 1.1. With this



scheme 1.1

very elegant route a variety of highly regular (93 to 98% head-to-tail) polymers was obtained in yields of 33 to 69%. These polymers exhibit enhanced conducting and optical properties when compared with the regiorandom materials. Conductivities up to 1000 Scm^{-1} for poly(3-dodecylthiophene) have been found, whereas for the regiorandom material the conductivity is limited to 20 Scm^{-1}. The maximum absorption increases 14 nm to 450 nm in solution and even more dramatically from 480 nm to 526 nm in the solid state. X-ray analysis indicates a crystalline and self-assembled structure and a well-defined distance between the polymer chains. Cyclic voltammetry exhibits two oxidation potentials versus one broad oxidation potential for the regiorandom poly(3-alkylthiophene)s. Zinc instead of magnesium has been used in the nickel[41,42] or palladium[43] catalyzed polymerizations. The use of $Ni(dppp)Cl_2$ affords regioregular polythiophenes[44] with band gaps as low as 1.7 eV[45], whereas regiorandom polythiophenes have bandgaps in the order of 2 to 2.2 eV. Besides the nickel(II) complexes the use of zerovalent nickel has been described[46,47]. In this case the dihalothiophene is coupled without being transformed to the

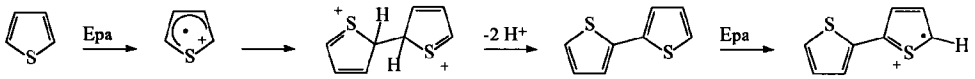
35 Mao, H.; Holdcroft, S. *Macromolecules* **1992**, *25*, 554.
36 Mao, H.; Xu. B.; Holdcroft, S. *Macromolecules* **1993**, *26*, 1163.
37 Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374.
38 Kumada, M.; Tamao, K.; Sumitani, K. *Org. Synth.* **1978**, *58*, 127.
39 McCullough, R. D.; Lowe, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, 70.
40 McCullough, R. D.; Lowe, R. D.; Jayarmam, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904.
41 Yamamoto, T.; Osakada, K.; Wakabayashi, T.; Yamamoto, A. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 671.
42 Ueda, M.; Miyaji, Y.; Ito, T.; Oba, Y.; Sone, T. *Macromolecules* **1991**, *24*, 2697.
43 Chen, T.-A.; O'Brien, R. A.; Riecke, R. D. *Macromolecules* **1993**, *26*, 3462.
44 Chen, T.-A.; Riecke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087.
45 Chen, T.-A.; Riecke, R. D. *Synth. Met.* **1993**, *60*, 175.
46 Yamamoto, T.; Maruyama, T.; Zhou, Z.-H.; Miyazaki, Y.; Kanbara, T.; Sanechika, K. *Synth. Met.* **1991**, *41-43*, 345.

organometallic intermediate. Consequently, the polymer has a regiorandom structure.

Due to the improved properties of regioregular 3-substituted polythiophenes, the polymerization based on the organometallic coupling of thiophene monomers is now by far the most interesting method. A number of polymers with functional groups in the side chain has been synthesized using this method as well; ethyleneglycol units give rise to conductivities[48] as high as 5500 Scm^{-1}. The high conductivity is believed to result from the oxygen containing side chains, which act like a crown ether and complex the dopant counterions[49]. Furthermore, these types of polythiophenes give rise to unique sensor properties[50]

1.2.1.2 Electrochemical synthesis

The synthesis of polythiophenes by electrochemical oxidation has been widely used since it was first described by Diaz[51]. Although the mechanism is not completely understood, the polymerization is proposed to proceed via the coupling of two radical cations, formed by the oxidation of the monomer as is outlined in scheme 1.2[52]. The



rearomatization of the dihydro dimer is the driving force in the coupling. The dimer, which has a lower oxidation potential than the monomer, is readily oxidized and undergoes further coupling. The polymer is deposited in its oxidized, and hence conducting, form onto the electrode, allowing the polymerization to proceed. This method has the advantage that during the polymerization homogeneous, stable films are formed. The films can be characterized by optical and electrochemical methods. Electrochemical polymerization has been used for the synthesis of unsubstituted polythiophene[53,54] and substituted

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47 Yamamoto, T.; Morita, A.; Miyazaki, Y.; Maruyama, T.; Wakayama, H.; Zhou, Z.-h.; Nakamura, Y.; Kanbara, T.; Sasaki. S.; Kubota, K. *Macromolecules* **1992**, *25*, 1214.

48 McCullough, R. D.; Williams, S.P. *J. Am. Chem. Soc.* **1993**, *115*, 11608.

49 McCullough, R. D.; Williams, S. P.; Jayaraman, M. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1994**, *35*, 190.

50 Swager, T. M.; Marsella, M. J. *Adv. Mater.* **1994**, *6*, 595.

51 Diaz, A. *Chem. Scr.* **1981**, *17*, 145.

52 for a detailed discussion see: Roncali, J. *Chem. Rev.* **1992**, *92*, 711.

53 Tourillon, G.; Garnier, F. *J. Electroanal. Chem.* **1982**, *135*, 173.

54 Kaneto, K.; Kohno, Y.; Yoshino, K.; Inuishi, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 382.

polythiophenes including poly-(3-methylthiophene)[55], poly-(3-ethylthiophene)[56] and of a number of different soluble poly-(3-alkylthiophenes)[57,58]. However, in all cases reported sofar, the polymers obtained possess a regiorandom structure.

In addition to alkyl substituted polymers, a variety of polythiophenes containing other functionalities have been synthesized by electrochemical polymerization. Oxygen containing substituents have also been used, including methoxy[59] and polyethers[60] with conductivities as high as 1050 Scm^{-1}. A highly transparent conducting polymer has been found by the polymerization of 3,4-ethylenedioxy thiophene[61]. Polyfluoroalkyl substituted polythiophenes have also been synthesized[62], while water-soluble, self-doped polythiophenes have been prepared by the introduction of ionic groups in the side chain[63,64,65,66].

Thiophene oligomers like bithienyls[67] and terthienyls[27], with a lower oxidation potential relative to thiophene (1.2-1.3 V and 1 V, respectively, versus 1.7 V for 3-butyl thiophene) have been used as monomers. An advantage of the lower oxidation potential is that a lower potential can be applied during polymerization decreasing the possibility of overoxidation. Nevertheless, the materials do not exhibit properties surpassing that of polymers prepared from thiophene monomers. Silyl-substituted thiophenes have been polymerized with the elimination of the silyl substituents[68].

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55 Yasser, A,; Roncali, J.; Garnier, F. *Macromolecules* **1989**, *22*, 804.
56 Sato, M.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc., Chem. Commun* **1985**, 713.
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61 Heywang, G.; Jonas, F. *Adv. Mater.* **1992**, *4*, 116.
62 Ritter, S. K.; Noftle, R. E.; Ward, A. E. *Chem. Mat.* **1993**, *5*, 752.
63 Havinga, E. E.; van Horssen, L. W.; ten Hoeve, W.; Wynberg, H.; Meijer, E. W. *Polym. Bull.* **1987**, *18*, 277.
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65 Patil, A. O.; Ikenoue, Y.; Basescu, N.; Colaneri, N.; Chen, J.; Wudl. F.; Heeger, A. J. *Synth. Met.* **1987**, *20*, 151.
66 Bäuerle, P.; Gaudl, K.-U.; Würthner, F.; Sariciftci, N. S.; Neugebauer, H.; Mehring, M.; Zhong, C.; Doblhofer, K. *Adv. Mater.* **1990**, *2*, 490.
67 Arbizzani, C.; Barbarella, G.; Bongini, A.; Mastragostino, M.; Zambianchi, M. *Synth. Met.* **1992**, *52*, 329.
68 Masuda, H.; Taniki, Y.; Kaeriyama, K. *J. Polym. Sci. Part A: Polym. Chem.* **1992**, *30*, 1667.

1.2.1.3 Oxidative coupling

Conducting polythiophenes are formed in the oxidation of thiophene or bithienyl with arsenic(V) fluoride. The observation that the material can be reduced with ammonia clearly displays that polymerization has occurred[69]. Due to the poisonous properties of arsenic(V) fluoride the method is not very practical. A more convenient method has been developed by Yoshino et al.[70], by using iron(III) chloride as oxidizing agent and chloroform as solvent under anhydrous conditions. Subsequent reduction with ammonia provides the neutral polymer in good yields. The reaction is easily carried out and this method has now widely been employed in the synthesis of polythiophenes from thiophene with alkyl[71,72], alkoxy[19] and alkylsulphonic acid[73] substituents, bithienyl with two alkyl substituents[74,75], and one alkyl substituent[76]. The bithienyl monomer can also be polymerized using milder oxidants[77].

The oxidative coupling of thiophenes provides materials with higher molecular weights than the routes described above. However, in a study[78] a comparison has been made between hexylthiophene and the deuterated analog, which indicates that considerable crosslinking occurs through the alkyl side chains. Reaction temperatures below -20°C lead to a diminished degree of crosslinking and with this an increased yield of soluble 3-substituted polythiophenes. Although the polymers obtained by the iron(III) chloride oxidation of 3-substituted thiophenes exhibit a regiorandom structure, the polymerization of 3-(4-octylphenyl)thiophene by using a modified procedure has produced a polymer with a high degree of regioregularity[79]. However, this high regioregularity is a result of the phenyl substituent and is not solely due to the modified procedure.

Coupling of aromatic rings can be accomplished by the copper(II) chloride

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69 Koßmehl, G.; Chatzitheodorou, G. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 551.
70 Sugimoto, R.; Takeda, S.; Gu, H. B.; Yoshino, K. *Chem. Express* **1986**, *1*, 635.
71 Leclerc, M.; Diaz, F. M.; Wegner, G. *Makromol. Chem.* **1989**, *190*, 3105.
72 Österholm, J.-E.; Laakso, J.; Nyholm, P.; Isotalo, H.; Stubb, H.; Inganäs, O.; Salaneck, W. R. *Synth. Met.* **1989**, *28*, C435.
73 Ikenoue, Y.; Saida, Y.; Kira, M.; Tomozawa, H.; Yashima, H.; Kobayashi, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1694.
74 Souto Maior, R. M.; Hinkelmann, K.; Eckert, H.; Wudl, F. *Macromolecules* **1990**, *23*, 1268.
75 Zagórska, M.; Krische, B. *Polymer* **1990**, *31*, 1379.
76 Andersson, M. R.; Pei, Q.; Hjertberg, T.; Inganäs, O.; Wennerström, O.; Österholm, J.-E. *Synth. - Met.* **1993**, *55-57*, 1227.
77 Kaeriyama, K.; Masuda, H.; Shirakawa, H.; Akagi, K.; Suezawa, H.; Hirota, M. *Polym. Mater. Sci. Eng.* **1991**, *64*, 212.
78 Gautun, O. R.; Carlsen, P. H. J.; Samuelsen, E. J.; Mårdalen, J. *Synth. Met.* **1993**, *58*, 115.
79 Andersson, M. R.; Selse, D.; Berggren, M.; Järvinen, H.; Hjertberg, T.; Inganäs, O.; Wennerström, O.; Österholm, J.-E.; *Macromolecules* **1994**, *27*, 6503.

oxidation of their lithium derivatives[80]. This has been applied to the synthesis poly-(3-methylthiophene)[81,82] and to polymers containing bithienyl units[83].

1.2.2 Polypyrrole

The first synthesis of polypyrrole, appreciating the conducting properties, was described in 1968[84]. Electrochemical oxidation of a pyrrole solution in 0.1 N sulfuric acid afforded a black conducting film. Improvements through the use of organic solvents and different electrolytes have been made[85,86] and the electrochemical method has been the most employed polymerization technique ever since. Oxidized polypyrrole is stable under ambient conditions and up to temperatures exceeding 300°C[86]. The neutral form of polypyrrole, on the other hand, has not been isolated and characterized, due to its extreme susceptibility to oxidation.

The electrochemical route to polypyrrole provides good quality films. Counterions have a considerable influence on the conductivity and mechanical properties[87]. Changing the counterion from oxalate to perchlorate increases the conductivity by a factor of hundred thousand[51]. Commercially available (BASF) polypyrrole with tosylate as counterion exhibits a conductivity of 15 Scm^{-1} and the stability of the material at ambient conditions is extremely good; a decrease of less than 15% per year is reported. Alkylsulfonates and phosphates has been used as electrolyte as well[88], and processable polymer blends are formed by using sulfonated polystyrene as counterions in the polymer.

The oxidation of a neutral polypyrrole film with chemical oxidizing agents increases the conductivity relatively to the electrochemical oxidized material[89]. 2,2'-Bipyrrole has been used as monomer, but the properties of the polymer obtained are

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80 Kauffman, T. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 291.

81 Amer, A.; Zimmer, H.; Mulligan, K. J.; Mark Jr, H. B.; Pons, S.; McAleer, J. F. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 77.

82 van Pham, C.; Czerwinski, A.; Zimmer, H.; Mark Jr, H. M. *J. Polym. Sci., Part C: Polym. Lett.* **1986**, *24*, 103.

83 Berlin, A.; Pagani, G. A.; Sannicolo, F. *Synth. Met.* **1987**, *18*, 157.

84 Dall'Olio, A.; Dascola, G.; Varacca, V.; Bocchi, V. *C. R. Acad. Sc.* **1968**, *C 267*, 433.

85 Diaz, A. F.; Kanazwa, K. K.; Gardini, G. P. *J. Chem. Soc., Chem. Commun.* **1979**, 635.

86 Kanazawa, K. K.; Diaz, A. F.; Gill, W.D.; Grant, P. M.; Street, G. B.; Gardini, G. P.; Kwak, J. F. *Synth. Met.* **1979/80** *1*, 329.

87 Qian, R.; Qiu, J.; Shen, D. *Synth. Met.* **1987**, *18*, 13.

88 Wernet, W.; Monkenbusch, M.; Wegner, G. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 193.

89 Street, G. B.; Clarke, T. C.; Krounbi, M.; Kanazawa, K.; Lee, V.; Pfluger, P.; Scott, J. C.; Weiser, G. *Mol. Cryst. Liq. Cryst.* **1982**, *83*, 253.

similar to the parent polymer obtained from pyrrole itself[90]. Pyrrole has been chemically polymerized with oxidants including sulfuric acid[91], bromine and iodine[92], copper(II) perchlorate[93] and iron(III) chloride[94].

Soluble polypyrrole can be prepared by the introduction of flexible side chains[60,95,96,97]. In contrast with the progress made in the synthesis of regioregular polythiophenes, all 3-substituted polypyrroles reported so far have a regiorandom structure. Substitution on the nitrogen affords a regular soluble polymer, however, the conductivity is reduced drastically, due to the strong steric interactions of the nitrogen substituent and the hydrogens at the 3- and 4-positions of the adjacent pyrrole ring. Both rings are forced to go out of plane resulting in a loss of conjugation and hence a reduced conductivity[98]. Although the differences between a 3-substituted polypyrrole and a N-substituted polypyrrole at first glance are small with regard to steric hindrance, their conductivities differ significantly, again showing the subtilities in the structure-property relationship. The chemical oxidative method has also been applied to 3-alkyl pyrroles[95,96] and to 3,4-dimethoxy pyrrole[99].

The introduction of sulfonic acid groups in the alkyl side chains affords water-soluble self-doped polypyrrole[63]. Using the sodium salt of the 3-alkylsulfonic acid pyrrole, the monomer acts as electrolyte for the electrochemical synthesis as well. A second long alkyl chain on the opposite side of the pyrrole ring affords a highly ordered lamellar polymer also soluble in chloroform[100]. Langmuir-Blodgett techniques have been used to improve the ordering of the polypyrrole films[101,102].

Structural defects like α,ß-couplings are inherent in oxidative polymerizations and to a minor extent can be present in the materials synthesized as described above. This failure to produce perfect 2,5-linked polypyrroles has been overcome by organometallic

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90 Lindenberger, H.; Schäfer-Siebert, D.; Roth, S.; Hanack, M. *Synth. Met.* **1987**, *18*, 37.

91 Salmon, M.; Kanazawa, K. K.; Diaz, A. F.; Krounbi, M. *J. Polym. Sci., Polym. Lett.* **1982**, *20*, 187.

92 Chan, H. S. O.; Munro, H. S.; Davies, C.; Kang, E. T. *Synth. Met.* **1988**, *22*, 365.

93 Castillo-Ortega, N. M.; Inoue, M. B.; Inoue, M. *Synth, Met.* **1989**, *28*, C65.

94 Lei, J.; Cai, Z.; Martin, C. R. *Synth. Met.* **1992**, *46*, 53.

95 Rühe, J.; Ezquerra, T. A.; Wegner, G. *Synth. Met.* **1989**, *28*, C177.

96 Masuda, H.; Tanaka, S.; Keariyama, K. *J. Chem. Soc., Chem. Commun.* **1989**, 725.

97 Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Synth. Met.* **1989**, *28*, C183.

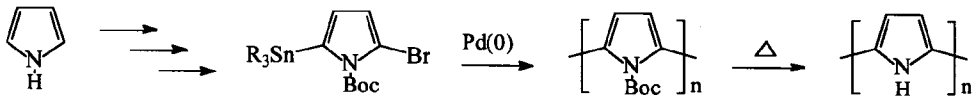
98 Kanazawa, K. K.; Diaz, A. F.; Geiss, R. H.; Gill, W. D.; Kwak, J. F.; Logan, J. A.; Rabolt, J. F.; Street, G. B. *J. Chem. Soc., Chem. Commun.* **1979**, 854.

99 Merz, A.; Schwarz, R.; Schropp, R. *Adv. Mater.* **1992**, *4*, 409.

100 Collard, D. M.; Fox, M. A. *J. Am. Chem. Soc.* **1991**, *113*, 9414.

101 Rahman, A. K. M.; Samuelson, L.; Minehan, D.; Clough, S.; Tripathy, S.; Inagaki, T.; Yang, X. Q.; Skotheim, T. A.; Okamoto, Y. *Synth. Met.* **1989**, *28*, C237.

102 Yang, X. Q.; Chen, J.; Hale, P. D.; Inagaki, T.; Skotheim, T. A.; Okamoto, Y.; Samuelson, L.; Tripathy, S.; Hong, K.; Rubner, M. F.; denBoer, M. L. *Synth. Met.* **1989**, *28*, C251.



scheme 1.3

polymerization techniques. Thus, pyrroles with a Boc protecting group at nitrogen have been polymerized via Stille coupling, affording a soluble non-planar precursor polymer that has been deprotected by thermal treatment (scheme 1.3). This polypyrrole, although of relative low molecular weight (approximately 3400), exhibits a perfect structure and is fully characterized[103]. N-Boc-protected pyrrole has also been polymerized by the Ullmann coupling of the dibromo species, affording the same polymers as obtained by the Stille chemistry[104]. A self-doped analog of polypyrrole has been obtained by means of the Ullmann coupling of N-butyl-2,5-dibromo-3,4-pyrroledione[105].

1.2.3 Polyaniline

The first report on the synthesis of polyaniline dates from 1834[106]. Polyanilines have been the subject of intensive research ever since. In the 1980's the conducting properties of polyaniline were recognized and the number of articles dealing with this conducting polymer has grown exponentially. Two main reasons for this growth, besides the scientific interest, are the low cost of aniline and the production process and the stability of the conducting form. In polyaniline there are a number of well-defined different oxidation states[107] (figure 1.4). The names were originally given by Green and

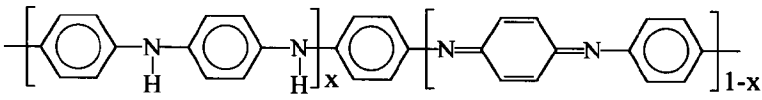


figure 1.4

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103 Martina, S.; Enkelmann, V.; Wegner, G.; Schlüter, A.-D. *Synth. Met.* **1992**, *51*, 299.

104 Groenendaal, L.; Peerlings, H. W. I.; Van Dongen, J. L. J.; Havinga, E. E.; Vekemans, J. A. J. M.; Meijer, E. W. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1994**, *35*, 194.

105 Brockmann, T. W.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 7435.

106 for a detailed historical review see: Geniès, E. M.; Boyle, A.; Lapkowski, M.; Tsintavis, C. *Synth. Met.* **1990**, *36*, 139.

107 Pandey, S. S.; Annapoorni, S.; Malhotra, B. D. *Macromolecules* **1993**, *26*, 3190.

Woodhead[108]; the term emeraldine must derive from the emerald green color of the base. The different states range from the fully reduced leucoemeraldine (x=1), protoemeraldine (x=0.75), emeraldine (x=0.5) and nigraniline (x=0.25) to the fully oxidized state pernigraniline (x=0) (figure 1.4). Unlike in most other polyaromatics, the fully oxidized state in polyaniline is not conducting. As a matter of fact none of the above described states is conducting. Polyaniline becomes conducting when the moderately oxidized states and in particular the emeraldine base (x=0.5) are protonated to generate the charge carriers. This is called 'protonic acid doping'[109]. Polyaniline is unique is this respect; no electrons need to be added to the insulating material to become conducting. The different oxidation states of polyaniline can be doped with oxidants such as iodine, but the conductivity is lower compared to the proton acid doping[110]. The conducting mechanism is believed to be of the polaron type; the protonated emeraldine consists of a delocalized poly(semiquinone radical cation)[111,112]. The conductivity is affected by the water content; completely dry samples are five times less conductive than samples containing some water[113]. The emeraldine base is soluble in N-methylpyrrolidone[114], but protonated polyaniline is insoluble in organic solvents and only soluble in aqueous acids. Substitution of the aniline monomer with alkyl or alkoxy groups improves the solubility in organic solvents, but has a negative influence on the conductivity[107,115,116]. The position of the substituent has an influence on the polymerization. The ortho and meta isomers give the same polymer, but it turned out that the reactivity of the meta isomer is considerably lower, resulting in a lower yield[115]. Self-doped polyaniline, containing sulfonic acid substituents, has been synthesized by sulfonation of the emeraldine base[117].

A different approach to produce soluble polyaniline is the use of n-alkyl sulfonic acids as proton donor; polyaniline doped with n-dodecylsulfonic acid does indeed give soluble and highly conducting materials[118,119]. Stable thin films of polyaniline that can be

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108 Green, A. G.; Woodhead, A. E. *J. Chem. Soc.* **1910**, *97*, 2388.
109 Chiang, J.-C.; MacDiarmid, A. G. *Synth. Met.* **1986**, *13*, 193.
110 Wang, L.; Jing, X.; Wang, F. *Synth. Met.* **1991**, *41-43*, 739.
111 MacDiarmid, A. G.; Chiang, J. C.; Richter, A. F.; Epstein, A. J. *Synth. Met.* **1987**, *18*, 285.
112 Epstein, A. J.; Ginder, J. M.; Zuo, F.; Bigelow, R. W.; oo, H.-S.; Tanner, D. B.; Richter, A. F.; Huang,W.-S.; MacDiarmid, A. G. *Synth. Met.* **1987**, *18*, 303.
113 Scherr, E. M.; MacDiarmid, A. G.; Manohar, S. K.; Masters, J. G.; Sun, Y.; Tang, X.; Druy, M. A.; Glatkowski, P. J.; Cajipe, V. B.; Fischer, J. E.; Cromack, K. R.; Jozefowitcz, M. E.; Ginder, J. M.; McCall, R. P.; Epstein, A. J. *Synth. Met.* **1991**, *41-43*, 735.
114 Angelopoulos, M.; Ray, A.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1987**, *21*, 21.
115 Leclerc, M.; Guay, J.; Dao, L. H. *Macromolecules* **1989**, *22*, 649.
116 MacInnes, D.; Funt,B. L. *Synth. Met.* **1988**, *25*, 235.
117 Yue, J.; Epstein, A. J. *J. Am. Chem. Soc.* **1990**, *112*, 2800.
118 Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1992**, *48*, 91.
119 Klavetter, F. L.; Cao, Y. *Synth. Met.* **1993**, *55-57*, 989.

processed out of solution are made from the emeraldine base and camphorsulfonic acid as dopant. m-Cresol as cosolvent is essential for obtaining a chiral crystalline structure[120].

Oxidation of aniline is the most widely employed synthetic route to polyaniline and can be performed either electrochemically or chemically, and is usually carried out in acidic media. The electrochemical method was originally developed by Letheby as a test for the determination of small quantities of aniline[121]. The method has been improved since[122,123,124] and also has been applied to alkyl[115,125] ,alkoxy[116] and dimethoxy[126] substituted anilines, the latter exhibiting a conductivity comparable to polyaniline. Although chemical oxidation is usually carried out in acidic aqueous environments with an oxidizing agent such as ammonium persulfate[109,117], it has also been preformed in chloroform using tetrabutyl ammonium periodate[119]. Alkyl[115,125] and alkoxy[107,116] substituted polyanilines have been prepared by using the chemical method. It has been stated that in polyaniline crosslinking occurs during electrochemical synthesis due to the applied potential[127], but non-oxidative synthesized polyaniline exhibiting the same properties indicated a fully linear structure[128]. Polyaniline is crosslinked when the emeraldine base is heated to 300°C[113].

Although no data are available concerning the health risks of polyaniline, the possible occurrence of benzidine moieties, which are well-known carcinogens[129], indicates that care should be exercised in handling polyaniline.

1.2.4 Other heterocyclic polymers

In the field of the conducting and π-conjugated heterocyclic polymers by far the most attention has been paid to the polymeric systems described above. However, a variety of other polymers containing heterocyclic rings have been synthesized and studied as well.

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120 Havinga, E. E. Bouman, M. M.; Meijer, E. W.; Pomp, A.; Simenon, M. M. J. *Synth. Met* **1994**, *66*, 93.

121 Letheby, H. *J. Chem. Soc.* **1862**, *15*, 161.

122 Mohilner, D. M.; Adams, R. H.; Argersinger jr., W. J. *J. Am. Chem. Soc.* **1962**, *84*, 3618.

123 Diaz, A. F.; Logan, J. A.; *J. Electoanal. Chem.* **1980**, *111*, 111.

124 Wang, B.; Tang, J.; Wang, F. *Synth. Met.* **1986**, *13*, 329.

125 Wei, Y.; Focke, W. W.; Wnek, G. E.; Ray, A.; MacDiarmid, A. G. *J. Phys. Chem.* **1989**, *93*, 495.

126 Zotti, G.; Comisso, N.; D'Aprano, G.; Leclerc, M. *Adv. Mater.* **1992**, *4*, 749.

127 Kitani, A.; Kaya, M.; Yano, J.; Yoshikawa, K.; Sasaki, K. *Synth. Met.* **1987**, *18*, 341.

128 Vachon, D.; Angus jr., R. O.; Lu, F. L.; Nowak, M.; Schaffer, H.; Wudl, F.; Heeger, A. J. *Synth. Met.* **1987**, *18*, 297.

129 Armstrong, R. W. In Howe, G. M.; Loraine, J. A. Eds.; *Environmental Medicine* 2d. ed. William Heinemann Medical Books London **1980**; p 182.

In the following section some of the most promising classes with respect to improved material properties are discussed.

1.2.4.1 Small Band Gap Polymers

A promising class of materials in the search for organic metals is the class of small band gap polymers. Next to high conductivity, these systems are believed to be transparent in their conducting form, and when the band gap approaches zero these materials will exhibit metallic properties. In 1984, Wudl et al.[130] published the synthesis of poly(isothia-naphthene) (PITN) with a band gap of 1 eV (for comparison: polythiophene has a band gap of 2 eV). Limited synthetic work has been performed on these kind of systems since, but recently the synthesis of a substituted PITN and poly(2,3-dihexylthieno[3,4-b]pyrazine have been published[131]. The small band gap is believed to arise from the relatively large contribution of the quinoid structure in the polymer[132]. Calculations have shown that a copolymer of thiophene and isonaphtothiophene will exhibit a band gap of 0.5 eV[133].

Polycyclopenta[2,1-b;3,4-b']dithiophen-4-one has a band gap of 1.2 eV due to its reduced aromatic character[134]. Polymerization of terthienyl with one fused thiadiazole unit at the central thiophene ring resulted in a polymer with a band gap of 0.9 eV, arising to some extent from the nitrogen sulfur interactions, which improve the intrachain charge mobility[135]. The synthesis of a polymer with a band gap as low as 0.5 eV based on the idea of bringing together positive and negative charges has been published by Havinga et al[136]. Polysquaranes and polycroconanes have been synthesized by using a condensation polymerization. Furthermore, Jenekhe[137,138] suggested that the introduction of methine groups between thiophene moieties would provide polymers with band gaps as low as 0.75 eV. Others, however, have contradicted this conclusion[139].

To put the importance of the band gap in perspective, none of these small band gap materials have conductivities surpassing the conventional polymers like polythiophene

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130 Wudl, F.; Kobayashi, M.; Heeger, A. J. *J. Org. Chem.* **1984**, *49*, 3382.
131 Pomerantz, M.; Chaloner-Gill, B.; Harding, L. O.; Tseng, J. J.; Pomerantz, W. J. *Synth. Met.* **1993**, *55-57*, 960.
132 Bredas, J. L.; Heeger, A. J.; Wudl, F. *J. Chem. Phys.* **1986**, *85*, 4673.
133 Kürti, J.; Surján, P. R.; Kertesz, M. *J. Am. Chem. Soc.* **1991**, *113*, 9865.
134 Lambert, T. L.; Ferraris, J. P. *J. Chem. Soc., Chem. Commun.* **1991**, 752.
135 Tanaka, S.; Yamashita, Y. *Synth. Met.* **1993**, *55-57*, 1251.
136 Havinga, E. E.; ten Hoeve, W.; Wynberg, H. *Synth. Met.* **1993**, *55-57*, 299.
137 Jenekhe, S. A. *Nature* **1986**, *322*, 345.
138 Jenekhe, S. A. *Macromolecules* **1990**, *23*, 2848.
139 Patil, A. O.; Wudl, F. *Macromolecules* **1988**, *21*, 542.

and polyaniline[140].

1.2.4.2 Fused Monomers

Fused heterocyclic compounds including thieno[3,2-b]pyrrole[141], thieno[3,2-b]thiophene[142], dithieno[3,2-b;2',3'-d]thiophene[143], dihydro-benzodipyrroles[144] and dihydro-thienodipyrrole[144] have been polymerized electrochemically. Other nitrogen containing polymers such as poly(quinoxaline-5,8-diyl)s[145], and poly(quinoline-5,8 and 1,4-diyl)[146] have been synthesized by polymerization of the dibromo compounds with zerovalent nickel as catalyst. Dehydrogenative polycondensation of tetrahydroquinoline at elevated temperatures affords a highly conducting poly(quinoline-2,8-diyl)[147].

A special kind of fused polyaromatic is polyphenylene sulfide. The polymer has been synthesized by a number of methods including electrochemically from thiophenol[148], oxidative from phenylene disulfide[149] and chemically from 4,4'-dibromo phenylene disulfide with copper[150]. Upon oxidation with arsenic(V)fluoride in arsenic(III)fluoride the aromatic rings are coupled with forming the benzothiophene moiety[151]. Conductivities up to 200 Sm^{-1} have been reported. Finally, some results from studies of fused conjugated polymers based on dyes have been published[152,153]. These materials are claimed to be conducting without additional dopants.

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140 Meyer, W. H. *Adv. Mater.* **1993**, *5*, 254.

141 Lazzaroni, R.; Riga, J.; Verbist, J. J.; Cristiaens, L.; Renson, M. *J. Chem. Soc., Chem. Commun.* **1985**, 999.

142 Danieli, R.; Taliani, C.; Zamboni, R.; Giro, G.; Biserni, M.; Mastragostino, M.; Testoni, A. *Synth. Met.* **1986**, *13*, 325.

143 Jow, T. R.; Jen, K. Y.; Elsenbaumer, R. L.; Shacklette, L. W.; Angelopoulos, M.; Cava, M. P. *Synth. Met.* **1986**, *14*, 53.

144 Schiavon, G.; Zotti, G.; Berlin, A.; Pagani, G.; Sannicolò, F. *Synth. Met.* **1989**, *28*, C199.

145 Kanbara, T.; Yamamoto, T. *Macromolecules* **1993**, *26*, 3464.

146 Kanbara, T.; Saito, N.; Yamamoto, T.; Kubota, K. *Macromolecules* **1991**, *24*, 5883.

147 Chiang, L. Y.; Swirczewski, J. W.; Goshorn, D. P. *Synth. Met.* **1991**, *41-43*, 1425.

148 Tsuchida, e.; Nishide, H.; Yamamoto, K.; Yoshida, S. *Macromolecules* **1987**, *20*, 2315.

149 Tsuchida, E.; Yamamoto, K.; Nishide, H.; Yoshida, S. *Macromolecules* **1987**, *20*, 2030.

150 Handlovitz, C. E. *Macromol. Synth.* **1968-1969**, *3*, 131.

151 Shacklette, L. W.; Elsenbaumer, R. L.; Chance, R. R.; Eckhardt, H.; Frommer, J. E.; Baughman, R. H. *J. Chem. Phys.* **1981**, *75*, 1919.

152 Kossmehl, G. A. in *Handbook of Conducting Polymers,* Skotheim, T. Ed., Marcel Dekker, New York, **1986**, Vol 1, pp 393-396.

153 Kallitsis, J. K.; Martinez, F.; Naarmann, H. *Synth. Met.* **1993**, *55-57*, 773.

1.2.4.3 Other Homopolymers

Polypyridine has been synthesized through the homocoupling of dibromopyridine[154] or dibromobipyridine[155] with zerovalent nickel as catalyst. The polymers are soluble only in formic acid as is the methyl substituted polypyridine[156], but the introduction of hexyl groups induces solubility in other organic solvents as well[157]. A detailed discussion on the peculiar properties of these polypyridines have been published recently, reporting on the self-assembled structures[158]. Poly(pyrimidine-2,5-diyl)[159] has been prepared utilizing the same method. Other examples of heterocyclic homopolymers are polypyridazine[160] and polythiazole[161].

1.2.5 Poly(paraphenylene)

Poly(paraphenylene) can be reduced or oxidized to produce conducting materials with conductivities upto 500 Scm^{-1}. Both conducting species are highly sensitive towards water and oxygen, whereas neutral poly(paraphenylene) is stable, both thermodynamically and chemically[162]. For the synthesis of poly(paraphenylene) a number of different routes have been employed, namely: oxidative coupling, organometallic coupling and dehydrogenation of polycyclohexylenes. These methods will be discussed in sections 1.2.5.1 to 1.2.5.3 below.

1.2.5.1 Oxidative coupling

The first method reported for the synthesis of poly(paraphenylene) is the coupling of benzene by Lewis acid catalysis in the presence of an oxidant. In 1963 poly(paraphenylene) was synthesized by stirring benzene, aluminium chloride and copper(II) chloride yielding a insoluble light brown powder[163]. The most favored mecha-

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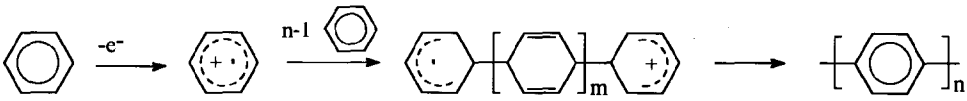
154 Yamamoto, T.; Ito, T.; Kubota, K. *Chem. Lett.* **1988**, 153.
155 Yamamoto, T.; Zhou, Z.; Kanbara, T.; Maruyama, T. *Chem. Lett.* **1990**, 223.
156 Maruyama, T.; Zhou, Z.-h.; Kubota, K; Yamamoto, T. *Chem. Lett.* **1992**, 643.
157 Maruyama, T.; Kubota, K.; Yamamoto, T. *Macromolecules* **1993**, *26*, 4055.
158 Yamamoto, T.; Maruyama, T.; Zhou, Z-h.; Ito, T.; Fukuda, T.; Yoneda, Y.; Begum, F.; Ikeda, T.; Sasaki, S.; Takezoe, H.; Fukuda, A.; Kubota, K. *J. Am. Chem. Soc.* **1994**, *116*, 4832.
159 Kanbara, T.; Kushida, N.; Saito, N.; Kuwajima, L.; Kubota, K.; Yamamoto, T. *Chem. Lett.* **1992**, 583.
160 Satoh, M.; Kaneto, K.; Yoshino, K. *J. Chem. Soc., Chem. Commun.* **1984**, 1627.
161 Bolognesi, A.; Catellani, M.; Destri, S.; Porzio, W. *Synt. Met.* **1987**, *18*, 129.
162 Kovacic, P.; Jones, M. B. *Chem. Rev.* **1987**, *87*, 357.
163 Kovacic, P.; Kyriakis, A. *J. Am. Chem. Soc.* **1963**, *85*, 454.



scheme 1.5

nism is shown in scheme 1.5. Benzene is oxidized to its radical cation which than propagates cationically. A second oxidation step produces the bis-cation, which looses two protons rearomatizing the terminal rings. Further oxidation of the dihydro structures finally affords the polymer[164]. Other Lewis acid/oxidant systems have been employed including AsF_3/AsF_5[165] and liquid SO_2 or sulfuric acid and aluminium chloride[166]. Poly(paraphenylene) has been synthesized by the electrochemical oxidation of benzene in solvents such as liquid SO_2[167] and concentrated sulfuric acid[168] or with the addition of Lewis acids including aluminium chloride[169], $CuCl_2/LiAsF_6$[170], and $BF_3.OEt_2$[171], affording polymeric films. To improve the solubility, poly(paraphenylene) has been sulfonated[172] and alkylated[173] with propyl halides to give materials with enhanced solubility.

1.2.5.2 Organometallic coupling

A number of different organometallic coupling methods have been used for the synthesis of poly(paraphenylene) including the Grignard cross-coupling of dihalobenzenes with a nickel catalyst[174,175], the cross coupling of dihalobenzenes with zero-valent nickel complexes[47], and the electrochemical reduction of dihalobenzenes activated by zero-valent nickel complexes[176,177]. Soluble poly(paraphenylene)s have been synthesized by the

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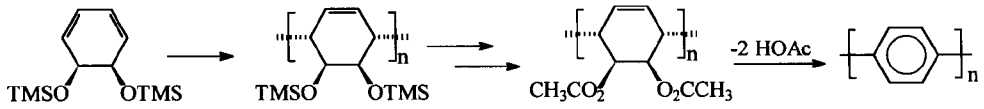
164 Milosevich, S.; Saichek, K.; Hinchey, L.; England, W. B.; Kovacic, P. *J. Am. Chem. Soc.* **1983**, *105,* 1088.
165 Aldissi, M.; Lepins, R. *J. Chem. Soc., Chem. Commun.* **1984**, 255.
166 Aeiyach, S.; Soubiran, S.; Lacaze, P. C.; Froyer, J.; Pelous, Y. *Synth. Met.* **1989**, *32,* 103.
167 Delamare, M.; Lacaze, P.-C.; Dumousseau, J.-Y.; Dubois, J.-E. *Electrochim. Acta* **1982**, *27,* 61.
168 Levi, M. D.; Pisarevskaya, E. Y.; Molodkina, E. B.; Danilov, A. I. *J. Chem. Soc., Chem. Commun.* **1992**, 149.
169 Kacriyama, K.; Sato, M.; Someto, K.; Tanaka, S. *J. Chem. Soc., Chem. Commun.* **1984**, 1199.
170 Sato, M.; Tanaka, M., Kaneto, K.; Yoshino, K. *Polym. Commun.* **1985**, *26,* 356.
171 Oshawa, T.; Inoue, T.; Takeda, S.; Kaneto, K.; Yoshino, K. *Polym. Commun.* **1986**, *27,* 61.
172 Kovacic, P.; Marchionna, V. J.; Koch, F. W.; Oziomek, J. *J. Org. Chem.* **1966**, *31,* 2467.
173 Jones, M. B.; Kovacic, P.; Lanska, D. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19,* 89.
174 Taylor, S.K.; Bennett, S. G.; Khoury, I.; Kovacic, P. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19,* 85.
175 Toshima, N.; Asakura, T. *Bull. Chem. Soc. Jpn.* **1993**, *66,* 948.
176 Fauvargue, J. F.; Petit, M. A.; Digua, A.; Savard, J. *Makromol. Chem.* **1985**, *186,* 2415.

introduction of flexible alkyl side chains utilizing the nickel catalyzed cross coupling reactions with magnesium or borium, although the improved solubility does not have a stimulating effect on the average degree of polymerization, which is of the order of thirteen[178]. Higher molecular weight polymers, with a average degree of polymerization of approximately hundred, have been obtained by the nickel(0) induced polymerization of methyl 2,5-dichlorobenzoate, which on saponification and decarboxylation was transformed into poly(paraphenylene)[179]. A polymerization without a transition metal catalyst has been achieved by the hexamethylphosphoramide induced polymerization of 1-bromo-4-lithiobenzene to provide soluble poly(paraphenylene)s with molecular weights up to 2000. These materials, however, consist of a considerable percentage (20-30%) meta linkages, which probably accounts for the remarkably high solubility[180].

1.2.5.3 Dehydrogenation of polycyclohexylenes

1,3-Cyclohexadiene has been polymerized in the presence of Ziegler type catalysts[181] or butyllithium[182] providing poly(1,3-cyclohexadiene), which can be converted to poly(paraphenylene) by oxidation with chloranil[181]. Diester derivatives of 5,6-dihydroxy-1,3-cyclohexadiene have been polymerized under radical conditions and the resulting polycyclohexylenes converted to poly(paraphenylene) by the application of heat[183,184]. These polymers, due to fracturing during pyrolysis, are of relative low molecular weight and contain some ortho likages. This route has been improved by Grubbs et al.[185] using bis-trimethylsilylethers as monomer and bis[(allyl)trifluoroacetonickel(II)] as catalyst, to yield the cis polycyclohexylene with an average degree of polymerization of 150. Transformation to the diester and pyrolysis afford poly(paraphenylene) (scheme 1.6).



scheme 1.6

177 Aboulkassim, A.; Chevrot, C. *Polymer* **1993**, *34*, 401.
178 Rehahn, M.; Schlüter, A.-D.; Wegner, G.; Feast, W. J. *Polymer* **1989**, *30*, 1054.
179 Chaturvedi, V.; Tanaka, S.; Kaeriyama, K. *Macromolecules* **1993**, *26*, 2607.
180 Tour, J. M.; Stephens, E. B. *J. Am. Chem. Soc.* **1991**, *113*, 2309.
181 Frey, D. A.; Hasegawa, M.; Marvel, C. S. *J. Polym. Sci., Part A* **1963**, *1*, 2057.
182 Cassidy, P. E.; Marvel, C. S. *Macromol. Synth.* **1972**, *4*, 7.
183 Ballard, D. G. H.; Curtis, A.; Shirley, I. M.; Taylor, S. C. *Macromolecules* **1988**, *21*, 294.
184 McKean, D. R.; Stille, J. K. *Macromolecules* **1987**, *20*, 1787.
185 Gin, D. L.; Conticello, V.P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3167.

1.2.6 Polyacetylene

The prototype of the simplest conjugated organic polymer is polyacetylene, which consists of alternating single and double carbon-carbon π-bonds. The first reports stem from the nineteenth century, but it was not until the early seventies that the conducting properties of the oxidized material were noted by Shirakawa[186]. This observation marks the start of the field "Conducting Polymers". Two main synthetic routes to polyacetylene have been employed, the Shirakawa route and the Luttinger[187] route. To improve the processability of the insoluble material Edwards and Feast[188] developed an alternative route for the synthesis of polyacetylene by preparing a soluble precursor polymer. Soluble polyacetylenes have been prepared by the introduction of flexible side chains. The different approaches are discussed in sections 1.2.6.1 to 1.2.6.4 below

1.2.6.1 Shirakawa route

Polymerization of acetylene by aluminium-titanium mixtures as catalyst was originally developed by Natta and optimalized by Shirakawa in the early seventies[186,189]. A typical polymerization procedure is as follows: A small amount of toluene is placed in the reaction vessel. First titanium tetra-n-butoxide and then triethylaluminium is added, with a aluminium-titanium ratio between 3.5 and 4. The catalyst solution is allowed to stand for 45 minutes at 20°C and then pure acetylene gas is introduced. The polymer obtained by this procedure is mainly cis. Increase of the temperature and the ageing time of the catalyst improves the conductivity[190], whereas the concentration and the aluminium-titanium ratio determines the morphology, which ranges from powder to film[191,192,193]. Almost pure trans polyacetylene is prepared on omission of the ageing step, and the use of a titanium-aluminium ratio of one[194]. The use of silicon oil instead of toluene is claimed to produce a polymer containing an equal amount of cis and trans moieties and a much

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186 Shirakawa, H,; Ikeda, S. *Polym. J.* **1971**, *2*, 231.
187 Luttinger, L. B. *J. Org. Chem.* **1962**, *27*, 1591.
188 Edwards, J. H.; Feast, W. J.; *Polymer* **1980**, *21*, 595.
189 Ito, T.; Shirakawa, H.; Ikeda, S. *J. Pol. Sci., Polym. Chem. Ed.* **1974**, *12*, 11.
190 Abadie, M. J. M.; Boukli-Hacene, S. M. *Eur. Polym. J.* **1988**, *24*, 251.
191 Whek, G. E.; Chien, J. C. W.; Karasz, F. E.; Druy, M. A.; Park, Y. W.; MacDiarmid, A. G.; Heeger, A, J. *J. Pol. Sci., Polym. Chem. Ed.* **1979**, *17*, 779.
192 Shirakawa, H.; Ikeda, S. *Synth. Met.* **1980**, *1*, 595.
193 Shelburne, J. A.; Baker, G. L. *Macromolecules* **1987**, *20*, 1212.
194 Baker, G. L.; Shelburne, J. A.; Bates, F. S. *J. Am. Chem. Soc.* **1986**, *108*, 7377.

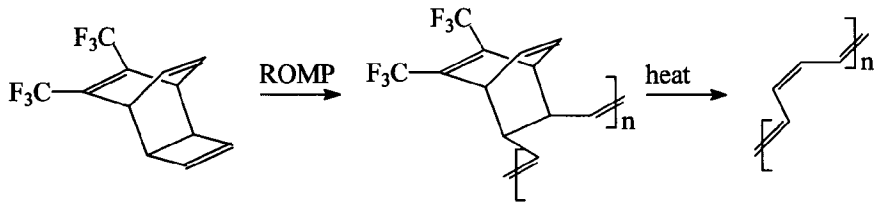
lower concentration of sp^3 carbon atoms[195]. Naarmann et al.[196] have developed the so-called "reducing agent method" where the addition of a reducing agent to the catalyst prior to the polymerization affords stretchable polyacetylene with conductivities of up to 10^5 Scm^{-1}. Tsukamoto[197] has prepared materials exhibiting equal or even higher conductivities treating the catalyst in a high boiling solvent, such as decalin, at temperatures around 200°C.

1.2.6.2 The Luttinger route

In the early sixties Luttinger[187] discovered that acetylene can be polymerized using group VIII metals and a hydride reductant as catalyst. With this method, polyacetylene powders are obtained. The importance of the route has been established by Enkelmann et al.[198] who found that these powders can be processed into films, either from suspensions or by moulding the powders. These films exhibited properties similar to the materials obtained by Shirakawa's method. The main advantage over Shirakawa's method is that it allows the polymerization to be carried out in the presence of water and oxygen. The best results are obtained using cobalt(II) nitrate and sodium borohydride[199]; the yields and crystallinity are increased by decreasing the reaction temperature[200].

1.2.6.3 Precursor route

The processibility of polyacetylene can be improved significantly by using soluble precursor polymers that are easily converted into the insoluble polyacetylene. Feast et



scheme 1.7

195 Haberkorn, H.; Heckman, W.; Kohler, G.; Naarmann, H.; Schlag, J.; Simak, P.; Theophilou, N.; Voelkel, R. *Eur. Polym. J.* **1988**, *24*, 497.
196 Naarmann, H.; Theophilou, N. *Synth. Met.* **1987**, *22*, 1.
197 Tsukamoto, J. *Advances in Physics* **1992**, *41*, 509.
198 Enkelmann, V.; Muller, W.; Wegner, G. *Synth. Met.* **1980**, *1*, 185.
199 Enkelmann, V.; Lieser, G.; Muller, W.; Wegner, G. *Angew. Makromol. Chem.* **1981**, *94*, 105.
200 Frohner, J.; Wuckel, L. *Acta. Polym.* **1987**, *38*, 334.

al.[188,201] have developed a method where the initial polymer is converted to polyacetylene by the appliance of heat (scheme 1.7). Thus, 7,8-bis(trifluoromethyl)tricyclo[4.2.2.$0^{2,5}$] deca-3,7,9-triene is polymerized by ring opening metathesis polymerization (ROMP) to give the high molecular weight precursor polymer. The precursor polymer is soluble in common organic solvents and is easily converted into polyacetylene with the evolution of 1,2-bis(trifluoromethyl)benzene at slightly elevated temperatures. Even at room temperature it is possible to convert the precursor polymer (half life: 20 hours). The temperature of retro Diels-Alder reactions can be adjusted by changing the substituents. To improve the stability of the precursor polymer the original monomer has photochemically been converted into the pentacyclic isomer by UV irradiation[202]. Polymerization indeed yields a stable precursor polymer, but the exothermicity of the conversion reaction limits the applicability. Molecular weight control and polydispersities close to unity have been achieved using different catalysts in the ring opening metathesis polymerization[203]. A limitation of both precursor polymers is the production of volatile elimination products. An improvement with regard to the by-products has been made by Swager et al.[204], who have polymerized benzvalene by ring opening metathesis polymerization and converted the precursor polymer to polyacetylene by catalytic isomerization.

With their work, Edwards en Feast have introduced the use of precursor polymers in the field of conducting polymers. Furthermore, they have initiated an organic chemical approach with respect to the synthesis of π-conjugated polymers.

1.2.6.4 Soluble polyacetylenes

Polyacetylene prepared by the methods described above is insoluble and of low tractability. To improve the solubility, substituted acetylenes have been polymerized to yield soluble polyacetylenes that have one substituent on every two carbon atoms[205]. However, due to the steric repulsion between the adjacent side groups the conjugation length is diminished resulting in materials of significantly lower conductivities[206]. Grubbs

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201 Bott, D. C.; Brown, C. S.; Chai, C. K.; Walker, N. S.; Feast, W. J.; Foot, P. J. S.; Calvert, P. D.; Billingham, N. C.; Friend, R. H. *Synth. Met.* **1986**, *14*, 245.

202 Feast, W. J.; Winter, J. N. *J. Chem. Soc., Chem. Commun.* **1985**, 202.

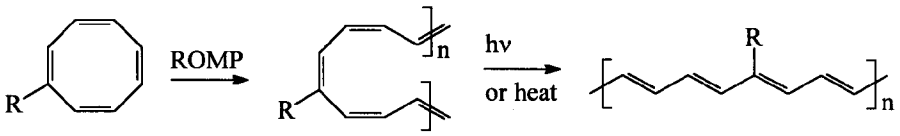
203 Knoll, K.; Schrock, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 7989.

204 Swager, T. M.; Dougherty, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2973.

205 Masuda, T.; Higashimura, T. *Acc. Chem. Res.* **1984**, *17*, 51.

206 Leclerc, M.; Prud'homme, R. E.; *Macromolecules* **1987**, *20*, 2153.

et al.[207,208] have synthesized polyacetylene with one side group on every eight carbon atoms by the ring opening metathesis polymerization of monosubstituted cyclooctatetraene derivatives (scheme 1.8). These materials are soluble and still exhibit high conductivities,

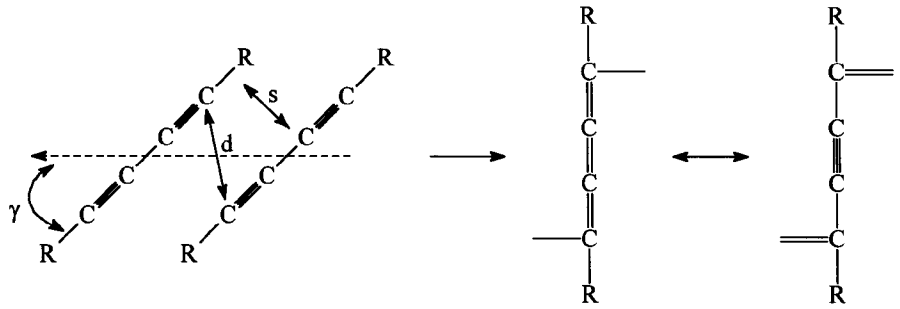


scheme 1.8

although the conjugation length has diminished. Especially for bulky substituents, such as the t-butyl group the decrease in conjugation is approximately 200 nm, emphasizing the importance of steric interactions of the solubilizing side groups. The introduction of chiral appendages results in the formation of a chiral main chain[209].

1.2.7 Polydiacetylenes

A special class of conjugated polymers consists of the polydiacetylenes; diacetylenes can be polymerized in the solid state either by irradiation or thermally yielding polymeric single crystals of large dimension. The photoreactivity of diacetylenes was discovered in 1882[210], but it was not until 1969 that the interesting macroscopic properties were recognized by Wegner[211]. Polymerization of diacetylenes proceeds by 1,4-additions to yield the conjugated polymer, which has two mesomeric forms (scheme 1.9).



scheme 1.9

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207 Gorman, C. B.; Ginsburg, E. J.; Sailor, M. J.; Moore, J. S.; Jozefiak, T. H.; Lewis, N. S.; Grubbs, R. H.; Marder, S. R.; Perry, J. W. *Synth. Met.* **1991**, *41-43*, 1033.

208 Gorman, C. B.; Ginsburg, E. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 1397.

209 Moore, J. S.; Gorman, C. B.; Grubbs, R. H. *J.Am. Chem. Soc.* **1991**, *113*, 1704.

210 Baeyer, A.; Landsberg, L. *Chem. Ber.* **1882**, *15*, 57.

211 Wegner, G. *Z. Naturforschung B* **1969**, *24*, 824.

It is proposed that the acetylenic structure is stabilized over the butatrienic structure by 12 kcal per C_4H_2 unit[212]. The packing of the monomer unit in the crystal is characterized by the separation of the monomers in the direction of the array (d) and the angle between the axis of the array and the diacetylenic rod (γ). Critical for the solid state polymerization seems to be the perpendicular distance between the units (s) and, since the end groups determine the monomer crystal structure, the nature of the end groups R.

Symmetrically disubstituted diacetylene monomers are usually synthesized by the oxidative coupling of terminal acetylenes with a cuprous salt and air[213], although other methods have been described[214]. The monomer most frequently used is 2,4-hexadiyne-1,6-diol, bis(p-toluene sulphonate) (R = $CH_2OSO_2C_6H_5CH_3$). The polymerization process is characterized by the occurence of an induction period, in which chain lengths of 10 to 20 units are formed, followed by a fast polymerization process above ten percent monomer conversion, to yield the single crystal polymers[215]. Although initially little work has been done on the molecular weight determination of polydiacetylenes, due to their insolubility or tendency to form aggregates, light scattering measurements have revealed an average molecular weight of about 800,000 g mol^{-1}, corresponding to 1500 monomeric units. This value was confirmed by GPC measurements. Other polydiacetylenes have molecular weights in the same range[216,217].

With the appropriate choice of end groups R, diacetylene monomeric films have been prepared via Langmuir-Blodgett techniques to afford structures of controlled thickness and orientation after polymerization[218]. Polymerization of mesogenic monomers yields polydiacetylenes which also exhibit liquid crystalline behaviour [216]. Although doping of highly crystalline polydiacetylene is not possible, conductivity measurements have been carried out on poorly crystalline polyacetylene films, but only moderate values have been obtained[219]. Of more interest are the optical properties of polydiacetylenes, including solvatochromism[216, 217], thermochromism[220] and non linearities[221,222], all

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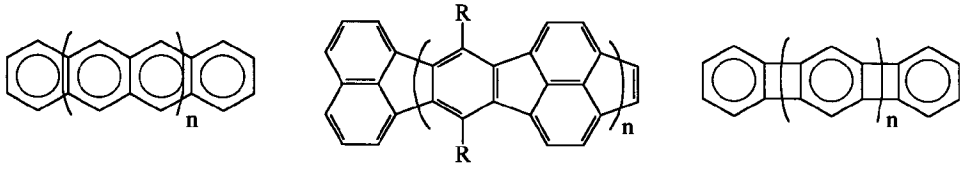
212 Karpfen, A. *J. Phys. C: Solid St. Phys.* **1980**, *13*, 5673.
213 Glaser, C. *Chem. Ber.* **1869**, *2*, 422.
214 Viehe, H. G. *Chem. Ber.* **1959**, *92*, 3064.
215 Baughman, R. H. *J. Chem. Phys.* **1978**, *68*, 3110.
216 Tsibouklis, J.; Campbell, C.; Wernick, A. R.; Shand, A. J.; Milburn, H. W. *Polym. Bull.* **1992**, *29*, 661.
217 Kim, W. H.; Kodali, N. B.; Kumar, J.; Tripathy, S. K. *Macromolucules* **1994**, *27*, 1819.
218 Tieke, B. *Adv. Polym. Sci.* **1985**, *71*, 79.
219 Se, K.; Ohnuma, H.; Kotaka, T. *Macromolecules* **1984**, *17*, 2126.
220 Sandman, D. J. *Trends Polym. Sci.* **1994**, *2*, 44.

characteristic for conjugated polymers.

1.2.8 Two-dimensional ladder structures

Ribbon-type conjugated polymers are known to have higher thermal stability and rigidity than their linear analogs[223]. Furthermore, this type of π-conjugated materials is expected to exhibit low band gaps[224]. The synthesis of these ladder or ribbon polymers is a demanding task and has been carried out by repetitive cycloadditions or by a two-step approach in which a linear polymer is transformed into a ladder polymer by ring-closure reactions. Ribbon-type polymers are obtained by Diels-Alder cycloaddition reactions of suitable monomers[225,226,227], but the conversion of the obtained materials into the fully conjugated polyacenes (figure 1.10.a) has been unsuccessful so far. A fully conjugated ladder polymer (figure 1.10.b) has been prepared by Diels-Alder cycloaddition reactions with the elimination of carbon monoxide and subsequent dehydrogenation[228]. The cocyclization of o-diethynylarenes with acetylenes has led to the formation of oligomer analogs of biphenylene[229,230] (figure 1.10.c). In the two-step approach a linear precursor



a b R= $-(CH_2)_{12}-$ c

figure 1.10

polymer, usually polyphenylene, with suitable functionalities, is prepared. The key step involves the ring closure affording the bridged phenylene ladder polymers (figure 1.11.a). Different types of bridges have been used, including methylene[231,232](x), vinylene[233](y),

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221 Sauteret, C.; Hermann, J.-P.; Frey, R.; Pradère, F.; Ducuing, J.; Baughman, R. H.; Chance, R. R. *Phys. Rev. Lett.* **1976**, *36*, 956.

222 Millburn, G. H. W.; Werninck, A.; Tsibouklis, J.; Bolton, E.; Thomson, G.; Shand, A. J. *Polymer* **1989**, *30*, 1004.

223 Yu, L.; Chen, M.; Dalton, L. R. *Chem. Mat.* **1990**, *2*, 649.

224 Müllen, K. *Pure & Appl. Chem.* **1993**, *65*, 89.

225 Schlüter, A.-D. *Adv. Mater.* **1991**, *3*, 282.

226 Godt, A.; Schlüter, A.-D. *Adv. Mater.* **1991**, *3*, 497.

227 Wegener, S.; Müllen, K. *Chem. Ber.* **1991**, *124*, 2101.

228 Schlüter A.-D.; Löffler, M.; Enkelmann, V. *Nature* **1994**, *368*, 831.

229 Hirthammer, M.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 2481.

230 Vollhardt, K. P. C. *Pure & Appl. Chem.* **1993**, *65*, 153.

231 Scherf, U.; Müllen, K. *Polymer Commun.* **1992**, *33*, 2443.

and imine[234](z) functionalities. The methylene bridged polymers require an additional dehydrogenation step to afford the conjugated ladder structure, which is not possible in all cases. Well-defined rulenes (figure 1.11.b) of high molecular weight have not been prepared yet, but some oligomers can be synthesized from oligonaphthylenes by subsequent anionic and cationic cyclization[235].

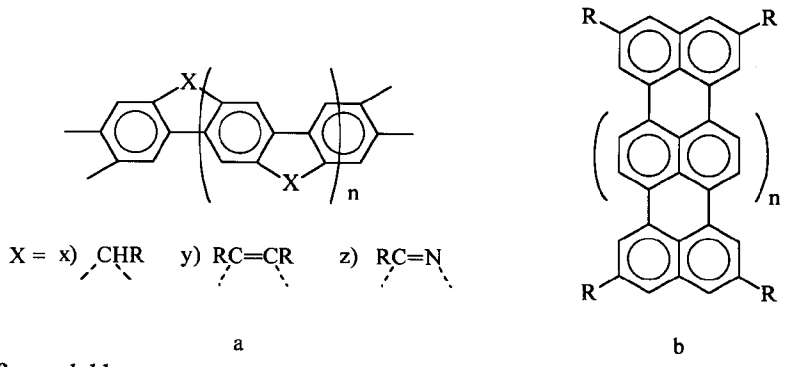

figure 1.11

The conjugation length of the ribbon-type polymers shows an increase (of more than 100 nm) relative to the linear parent compounds, as could be expected from the increase in co-planarity. Absorption values of over 600 nm, however, have only been obtained for the oligorulenes[235] and the dehydrogenated methylene bridged polyphenylenes[231], indicating that only a limited number of these materials indeed has low band gaps. On the other hand, some of the ladder polymers have been oxidized producing highly stable radical cations[236].

1.2.9 Phenylene-heteroarene copolymers

The synthesis of phenylene-heteroarene copolymers enables the investigator to combine the properties of the different homopolymers into one material, increasing the scope of potential applications. Alternating copolymers combine these properties more efficiently than copolymers with a random distribution, but their preparation requires

232 Scherf, U.; Müllen, K. *Macromolecules* **1992**, *25*, 3546.
233 Chmil, K.; Scherf, U. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 217.
234 Tour, J.; Lamba, J. J. S. *J. Am. Chem. Soc.* **1993**, *115*, 4935.
235 Koch, K.-H.; Müllen, K. *Chem. Ber.* **1991**, *124*, 2091.
236 Scherf, U.; Bohnen, A. Müllen, K. *Makromol. Chem.* **1992**, *193*, 1127.

selective polymerization techniques. The synthesis of such copolymers, both alternating and random, has received relative little attention. This will change due to the increasing interest in small band gap polymers (see section 1.2.4.1). The idea of using copolymers to introduce alternating structures of electron-rich and electron-poor moieties has emerged. Three synthetic routes have been developed: (1) direct polymerization of the different aromatics by either oxidative or chemical coupling methods, (2) ring closure of precursor polymers, and (3) polymerization of a monomer that already contains the desired array of units. The different strategies are outlined in sections 1.2.9.1 to 1.2.9.3.

1.2.9.1 Direct polymerization

Oxidative copolymerization requires monomers having similar oxidation potentials, otherwise the material obtained will be a mixture of both homopolymers or at best have a block structure. This limits the oxidative approach, which, however, has been used for a pyrrole-thiophene copolymer, prepared by the electrochemical polymerization of α-ter-thienyl and pyrrole[237], which have oxidation potentials of 1 V and 0.8 V, respectively. The chemical route is much more general; the reaction of a bis-metallated and a dihalo aromatic species, either of which may contain the heterocyclic ring, using palladium- or nickel-catalysts yields a completely alternating copolymer. Thus, heterocycles such as thiophene, selenophene and pyridine have been coupled with benzene and biphenyl using magnesium and nickel[238,239]. Thiophene and furan have been coupled with benzene and substituted benzenes using zinc and palladium[240,241], and alkoxy-substituted benzenes and thiophene have been coupled via the Stille reaction using tin and palladium[242]. The bromo\boronic acid coupling has been used in the coupling of alkyl substituted benzenes with Boc-protected pyrroles[243]. Zerovalent nickel has been used as catalyst in the copolymerization of thiophene with benzene[244] and pyridine[245,246]. The absence of organometallic monomers in this type of polymerization gives rise to materials have a random

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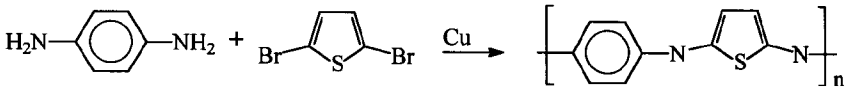
237 Inganäs, O.; Liedberg, B.; Chang-Ru, W.; Wynberg, H. *Synth. Met.* **1985**, *11*, 239.
238 Montheard, J. P.; Pascal, T.; Seytre, G.; Steffan-Boiteux, G.; Douillard, A. *Synth. Met.* **1984**, *9*, 389.
239 Monthéard, J. P.; Pascal, T.; Seytre, G.; Boiteux, G. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 679.
240 Pelter, A.; Rowlands, M.; Jenkins, H. *Tetrahedron Lett.* **1987**, *28*, 5213.
241 Pelter, A.; Maud, J. M.; Jenkins, I.; Sadeka, C.; Coles, G. *Tetrahedron Lett.* **1989**, *30*, 3461.
242 Bao, Z.; Chan, W.; Yu, L. *Chem. Mater.* **1993**, *5*, 2.
243 Martina, S.; Schlüter, A.-D. *Macromolecules* **1992**, *25*, 3607.
244 Czerwiński, W.; Nřcker, N.; Fink, J. *Synth. Met.* **1988**, *25*, 71.
245 Yamamoto, T.; Miyazaki, Y.; Fukuda, T.; Zhou, Z.; Maruyama, T.; Kanbara, T.; Osakada, K. *Synth. Met.* **1993**, *55-57*, 1214.
246 Yamamoto, T.; Zhou, Z.-H.; Maruyama, T.; Kanbara, T. *Synth. Met.* **1993**, *55-57*, 1209.

structure.

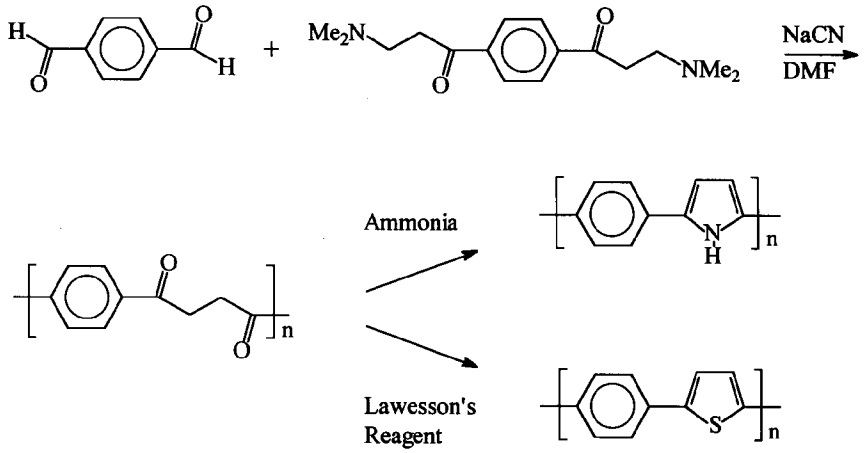
Dibromothiophene and p-phenylene diamine have been coupled under Ullmann conditions to give a copolymer of aniline and thiophene[247] (scheme 1.12).



scheme 1.12

1.2.9.2 Precursor route

Thiophenes and pyrroles have been synthesized by the ring closure of diacetylenes with hydrogen sulfide[248] and primary amines[249], respectively, and from 1,4-diketones with Lawesson's reagent[250] and ammonium acetate[250], respectively. An alternating copolymer of phenylene and diacetylene or 1,4-diketone moieties offers the possibility of the synthesis of an alternating copolymer consisting of phenylene and thiophene or pyrrole rings. Thus, diethynylbenzene is coupled oxidatively, affording the phenylene diacetylene copolymer, containing approximately 10% of the undesired meta isomer. Upon ring



scheme 1.13

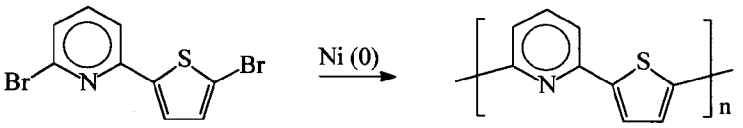
247 Polis, D. W.; Young, C. L.; McLean, M. R.; Dalton, L. R. *Macromolecules* **1990**, *23*, 3231.
248 Schulte, K. E.; Reisch, J.; Hörner, L. *Chem. Ber.* **1962**, *95*, 1943.
249 Reisch, J.; Schulte, K. E. *Angew. Chem.* **1961**, *7*, 241.
250 Wynberg, H.; Metselaar, J. *Synth. Commun.* **1984**, *14*, 1.

closure with hydrogen sulfide and aniline the phenylene-thiophene and the phenylene-N-phenylpyrrole copolymers are obtained[251].

The reaction of terephthaldehyde and the bis-Mannich base of 1,4-diacetylbenzene with sodium cyanide as catalyst in the Stetter[252] reaction affords polyphenylene-1,4-butanedione, which is the alternating phenylene 1,4-diketone polymer. Ring closure with Lawesson's reagent and ammonia affords the phenylene-thiophene and phenylene-pyrrole copolymers as outlined in scheme 1.13[253].

1.2.9.3 Oligomer polymerization

Oligomers may be polymerized oxidatively since the difference of the oxidation potentials of the different rings is no longer a restriction. A copolymer of thiophene and pyrrole has been prepared by the electrochemical polymerization of 2,2'-thienylpyrrole[254]. A number of other trimers containing thiophene, furan and N-methylpyrrole moieties have been polymerized oxidatively with $NOPF_6$ to provide the different copolymers[255]. Due to the unsymmetrical nature of the monomers, however, these copolymers are not completely alternating. An alternating copolymer of benzene and bithienyl units has been synthesized by the polymerization of 1,4-dithienylbenzenes either electrochemically[256] or oxidatively with iron(III) chloride[257]. Introdution of two alkyl or alkoxy substituents on the phenyl ring afforded regular and soluble polymers[258]. Polymers containing thiophene and pyridine units have been prepared from the dibromides using zerovalent nickel[259] (scheme 1.14).



scheme 1.14

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251 Bracke, W. *J. Polym. Sci., Part A-1* **1972**, *10*, 975.

252 Stetter, H.; Kuhlmann, H. *Org. React.* **1991**, *40*, 407.

253 Pouwer, K. L.; Vries, T. R.; Havinga, E. E.; Meijer, E. W.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1988**, 1432.

254 Naitoh, S. *Synth. Met.* **1987**, *18*, 237.

255 Joshi, M. V.; Hemler, C.; Cava, M. P.; Cain, J. L.; Bakker, M. G.; McKinley, A. J.; Metzger, R. M. *J. Chem. Soc., Perkin Trans 2* **1993**, 1081.

256 Danieli, R.; Ostoja, P.; Tiecco, M.; Zamboni, R.; Taliani, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1473.

257 Reynolds, J. R.; Ruiz, J. P.; Child, A. D.; Nayak, K.; Marynick, D. S. *Macromolecules* **1991**, *24*, 678.

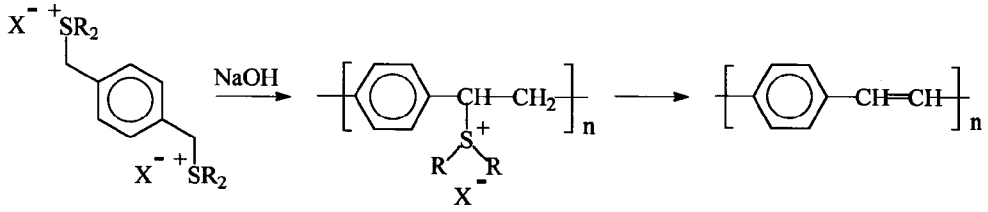
258 Ruiz, J. P.; Dharia, J. R.; Reynolds, J. R.; Buckley, L. J. *Macromolecules* **1992**, *25*, 849.

259 Yamamoto, T.; Miyazaki, Y.; Fukuda, T.; Zhou, Z.; Maruyama, T.; Kanbara, T.; Osakada, K. *Synth. Met.* **1993**, *55-57*, 1214.

1.2.10 Poly(arylene vinylene)s

Poly(arylene vinylene)s are perfectly alternating copolymers of trans-vinylene and aromatic units such as benzene[260], thiophene[261], naphthalene[262] and furan[263], and exhibit attractive material properties. Oriented poly(phenylene vinylene) (PPV) is highly crystalline[264], mechanically strong, environmentally stable and highly conducting, up to 5000 Scm^{-1}, when doped[265]. Furthermore, PPV's display large electroluminescence[266]

The first synthetic approaches to PPV's were based on dehydrohalogenation or Wittig condensation reactions, but the materials obtained are insoluble and mainly oligomeric[267,268]. With the development of a water soluble precursor polymer, high molecular weight polymers have been prepared and transformed into well defined poly(arylene vinylen)s[269] (scheme 1.15). The precursor polymer is synthesized by the base induced



scheme 1.15

polymerization of a bis-sulfonium salt in aqueous solution at low temperatures and with one equivalent of base. These mild polymerization conditions are required to suppress the uncontrolled formation of unsaturated segments by elimination of the sulphonium side chain. On heating, in an inert atmosphere to prevent oxidation of the vinylene carbons to carbonyls, the precursor is converted into poly(arylene vinylene) with the evolution of the sulfide and acid. Conversion into the conjugated polymer has also been achieved at room

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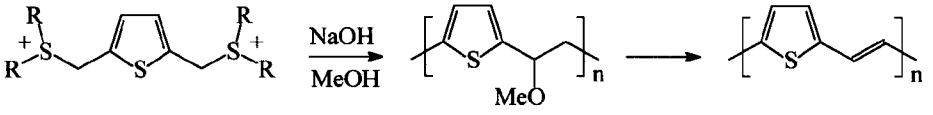
260 Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Polym. Commun.* **1984**, *25*, 327.
261 Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Polym. Commun.* **1987**, *28*, 229.
262 Antoun, S.; Gagnon, D. R.; Karasz, F. E.; Lenz, R. W. *J. Polym. Sci., Part C: Polym. Lett.* **1986**, *24*, 503.
263 Jen, K. Y.; Jow, T. R.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1987**, 1113.
264 Masse, M. A.; Martin, D. C.; Petermann, J. H.; Thomas, E. L.; Karasz, F. E. *J. Mater. Sci.* **1990**, *25*, 311.
265 Murase, I.; Ohnishi, T.; Nogushi, T.; Hirooka, M. *Synth. Met.* **1987**, *17*, 639.
266 Bradley, D. C. C. *Adv. Mater.* **1992**, *4*, 756.
267 Drefahl, V. G.; Kuhmstedt, R.; Oswald, H.; Horhold, H. H. *Makromol. Chem.* **1970**, *131*, 89.
268 Gourley, K. D.; Lillya, C. P.; Reynolds, J. R.; Chien, J. C. W. *Macromolecules* **1984**, *17*, 1025.
269 Wessling, R. A.; Zimmerman, R. G. **U.S. 3,401,152**: *C. A.* **1968**, *69*, 87735q. **U.S. 3,706,677**: *C. A.* **1973**, *78*, 85306n.

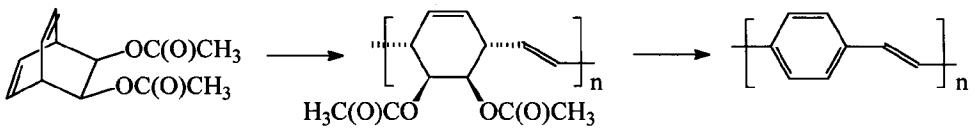
temperature by treatment of the precursor by strong acids and subsequent dedoping[270]. A poly(thienylene vinylene) precursor polymer soluble in organic solvents and of enhanced stability, and therefore processable[271], has been prepared by the use of methanol as cosolvent in the polymerization reaction. After termination of the reaction the temperature is increased to 20°C affording the methyl ether (scheme 1.16)[272]. Monomers containing



scheme 1.16

one[273], two[274] and four[275] methoxy substituents have been polymerized in order to improve the stability of oxidized poly(phenylene vinylene). Increasing the length of the side chain to six carbons leads to highly increased solubility[276]. The hexyloxy substituted precursor polyelectrolyte, however, is not soluble in water nor in organic solvents and partial elimination is necessary prior to further processing. The disadvantage of an insoluble precursor polymer can be eliminated by the conversion of the sulfonium salt to an alkyl ether yielding a soluble precursor polymer as well[277].

An alternative means for the synthesis of a soluble precursor polymer involves the ring opening metathesis polymerization of bicyclo[2,2,2]octadiene derivatives affording precursor polymers with the solubilizing functionality in the ring[278] (scheme 1.17). Soluble poly(phenylene vinylene) derivatives have been prepared by the direct coupling of substituted diiodobenzenes with divinylbenzene in the Heck coupling reaction using palladium acetate[279].



scheme 1.17

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270 Xia, Y.; MacDiarmid, A. G.; Epstein, A. J. *Adv. Mater.* **1994**, *6*, 293.
271 Tokito, S.; Smith, P.; Heeger, A. J. *Synth. Met.* **1990**, *36*, 183.
272 Yamada, S.; Tokito, S.; Tsutsui, T.; Saito, S. *J. Chem. Soc., Chem. Commun.* **1987**, 1448.
273 Liang, W. B.; Masse, M. A.; Karasz, F. E. *Polymer* **1992**, *33*, 3101.
274 Jen, K. Y.; Shacklette, L. W.; Elsenbaumer, R. L. *Synth. Met.* **1987**, *22*, 179.
275 Jin, J. I.; Park, C. K.; Shim, H. K. *Macromolecules* **1993**, *26*, 1799.
276 Askari, S. H.; Rughooputh, S. D.; Wudl, F. *Synth. Met.* **1989**, *29*, E129.
277 Han, C. C.; Elsenbaumer, R. L. *Synth. Met.* **1989**, *30*, 123.
278 Conticello, V. P.; Gin, D. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 9708.
279 Bao, Z.; Chen, Y.; Cai,R.; Yu, L. *Macromolecules* **1993**, *26*, 5281.

1.3 Synthesis of well-defined oligomers

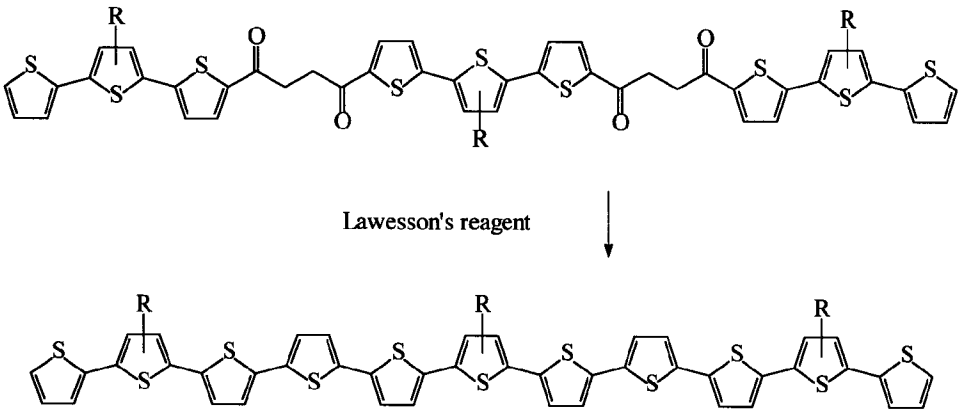
π-Conjugated oligomers have been the subject of a rapidly expanding field of research effort the last few years. The current interest is a consequence of the ability of well-defined oligomers to serve as model compounds for the corresponding polymers with respect to the synthesis, spectroscopic analysis and their physical properties. Furthermore, the possible use of oligothiophenes in applications has been established[280,281]. Garnier et al. have reported on an all-organic transistor using the unique properties of a self-assembled layer of a substituted sexithienyl. The high electron mobility of the oligomer, almost comparable to that of amorphous silicon, is used in this prototype device[282]. In the following section the most remarkable results on the synthesis and properties of well-defined oligomers are presented.

1.3.1 Thiophene oligomers

Of different conjugated oligomers the class of thiophenes has received by far the most attention, merely because several accessible synthetic routes are available, whereas the synthesis of for example oligopyrroles is very complicated. Oligothiophenes have been isolated from Marigolds[283] and synthesized some decades ago for the investigation of their nematicidal properties[284]. For the synthesis of well-defined thiophene oligomers a number of methods have been used[285]; the cross coupling reaction of a dihalo compound with organometallics like magnesium, zinc or tin with a palladium or nickel catalyst[286,287,288,289,290], the copper(II) chloride oxidation of an anion[291,292,293] and the ring

280 Garnier, F.; Horowitz, G.; Peng,X.; Fischou, D. *Adv. Mater.* **1990**, *2*, 592.
281 Xu, B.; Fischou, D.; Horowitz, G.; Garnier, F. *Adv. Mater.* **1991**, *3*, 150.
282 Garnier, F.; Hajlaoui, R.; Yasser, A.; Srivastava, P. *Science* **1994**, *265*, 1684.
283 Zechmeister, L.; Sease, J. W. *J. Am. Chem. Soc.* **1947**, *69*, 273.
284 Uhlenbroek, J. H.; Bijloo, J.D. *Rec. Trav. Chim. Pays-Bas* **1958**, *78*, 382.
285 for a review see: Nakayama, J.; Konishi, T.; Hoshino, M. *Heterocycles* **1988**, *27*, 1731.
286 van Pham, C.; Burkhardt, A.; Shabana, R.; Cunningham, D. D.; Mark jr., H. B.; Zimmer, H. *Phosphorus, Sulfur, and Silicon* **1989**, *46*, 153.
287 Waragai, K.; Hotta, S. *Synth. Met.* **1991**, *41-43*, 519.
288 Tour, J. M.; Wu, R. *Macromolecules* **1992**, *25*, 1901.
289 Bäuerle, P.; Pfau, F.; Schlupp, H.; Würtner, F.; Gaudl, K.-U.; Balparda Caro, M.; Fischer, P. *J. Chem. Soc., Perkin Trans. 2* **1993**, 489.
290 Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Chem. Mater.* **1993**, *5*, 430.
291 Garnier, F.; Horowitz, G.; Fischou,D. *Synth. Met.* **1989**, *28*, C705.
292 Yasser, A.; Delabouglise, D.; Hmyene, M.; Nessak, B.; Horowitz, G.; Garnier, F. *Adv. Mater.* **1992**, *4*, 490.

closure reaction of a 1,4-diketone with Lawesson's reagent[294,295,296] (scheme 1.18).



scheme 1.18

Oligothiophenes have been employed for conformational analysis. The structure of a few oligothiophenes containing two[297], three[298,299,300], four[301,302], five[303] and six[303,304] thiophene rings has been resolved by X-ray analysis. All compounds exhibit a nearly coplanar all-trans conformation, although the terminal rings may adopt a cis-cis conformation[303]. The all-head-to-tail substituted trimethyl-α-terthienyl derivative crystallizes in a chiral space group[300]. UV and NMR analysis together with calculations have shown that in solution unsubstituted quarterthiophene exhibits a planar cis-trans-cis conformation. The introduction of methyl substituents induces an equilibrium between planar cis and twisted trans-conformations and only when the substituents are head-to-head, the twisted trans-conformation is favoured, resulting in a considerable loss of conjugation[302,305].

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293 Faïd, K.; Leclerc, M. *J. Chem. Soc., Chem. Commun.* **1993**, 962.
294 ten Hoeve, W.; Wynberg, H.; Havinga, E. E.; Meijer, E. W. *J. Am. Chem. Soc.* **1991**, *113*, 5887.
295 Luo, T. H.; LeGoff, E. *J. Chin. Chem. Soc.* **1992**, *39*, 325.
296 Maud, J. M.; Haudry, P.; Llewellyn, G.; Vlahov, A.; Hepburn, A. R.; Marshall, J. M.; Goldie, D. M. *Synth. Met.* **1993**, *55-57*, 851.
297 Alemán, C.; Brillas, E.; Davies, A. G.; Fajarf, L.; Giró, D.; Juliá, L.; Péres, J. J.; Rius, J. *J. Org. Chem.* **1993**, *58*, 3091.
298 Van Bolhuis, F.; Wynberg, H.; Havinga, E. E.; Meijer, E. W.; Staring, E. G. J.; *Synth. Met.* **1989**, *30*, 381.
299 Kankare, J.; Lukkari, J.; Pasanen, P.; Sillanpää, R.; Laine, H.; Harmaa, K.; Visy, C. *Macromolecules* **1994**, *27*, 4327.
300 Barbarella, G.; Zambianchi, M.; Bongini, A.; Antolini, L. *Adv. Mater.* **1994**, *6*, 561.
301 Hotta, S; Waragai, K. *J. Mater. Chem.* **1991**, *1*, 835.
302 Barbarella, G.; Zambianchi, M.; Bongini, A.; Antolini, L. *Adv. Mater.* **1992**, *4*, 282.
303 liao, J.-H.; Benz, M.; LeGoff, E.; Kanatzidis, M. G. *Adv. Mater.* **1994**, *6*, 135.
304 Herrema, J. K.; Wildeman, J.; van Bolhuis, F.; Hadziioannou, G. *Synth. Met.* **1993**, *60*, 239.
305 Barbarella, G.; Bongini, A.; Zambianchi, M. *Adv. Mater.* **1991**, *3*, 494.

The use of oligomers containing more than six thiophene rings is restricted to substituted compounds due to the insolubility of the unsubstituted oligomers. Most of the oligomers differ from the substituted polythiophenes in their substitution pattern; they do not contain one substituent on every ring as is the case in most polythiophenes. Upon oxidation some of the shorter oligomers, up to six thiophene rings, were found to polymerize[306], so the reported[307] high conductivities of some of these oligomers are probably due to some polymeric material. Oligomers containing more than 6 thiophene rings do not polymerize, and it has been found that polymers made up of 11 or 12 thiophene rings[292,294,306] exhibit conductivities of 5-20 Scm^{-1} in the same range of that of polythiophene. Optical measurements show λ_{max} values that exceed polythiophene[292,306,308], but this is mainly due to a decrease of steric hindrance in the oligomers having less substituents. Extrapolation of these values results in a λ_{max} for polythiophene of 537 or 538 nm.[292,308], implying that the perfect polythiophene has not been synthesized yet.

A number of oligothiophenes have been employed in the investigation of the nature of the different oxidation states in polythiophene. Oxidation of oligothiophenes proceeds in two steps; the first is the formation of a radical cation (the analog of the polaron state in conjugated polymers), which exhibits a strong ESR signal. The dimerization of these radical cations to form diamagnetic π-dimers has been observed[309,310,311]. In the second step of the oxidation the radical cation is interconverted to the diamagnetic dication (the bipolaron analog). Although it has been reported that the oligomers must consist of at least six thiophene rings to undergo the second oxidation step[312], this claim is at variance with other results[287,308,313].

Langmuir-Blodget films of oligothiophenes and in particular 2,2',5',2''-terthienyl derivatives exhibit large dielectric constants and high conductivities with or even without additional dopants[314]. Oligothiophenes exhibit other characteristics that are known from

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306 Havinga, E. E.; Rotte, I.; Meijer, E. W.; ten Hoeve, W.; Wynberg, H. *Synth. Met.* **1991**, *41-43*, 473.

307 Cao, Y.; Guo, D.; Pang, M.; Qian, R. *Synth. Met.* **1987**, *18*, 189.

308 Bäuerle, P. *Adv. Mater.* **1992**, *4*, 102.

309 Hill, M. G.; Mann, K. R.; Miller, L. L.; Penneau, J.-F. *J. Am. Chem. Soc.* **1992**, *114*, 2728.

310 Bäuerle, P.; Segelbacher, U.; Gaudl, K.-U.; Huttenlocher, D.; Mehring, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 76.

311 Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Chem. Mater.* **1993**, *5*, 620.

312 Fichou, D.; Xu, B.; Horowitz, G.; Garnier, F. *Synth. Met.* **1991**, *41-43*, 463.

313 Guay, J.; Diaz, A.; Wu, R.; Tour, J. M.; Dao, L. H. *Chem. Mater.* **1992**, *4*, 254.

314 Nakahara, H.; Nakayama, J.; Hoshino, M.; Fukuda, K. *Thin Solid Films* **1988**, *160*, 87.

polythiophenes, such as thermochromism[293] and hyperpolarizability[315].

1.3.2 Other oligomers

In sharp contrast with the oligothiophene series, the reports on other π-conjugated oligomers are limited, owing to the difficulties encountered in the synthesis of these well-defined oligomers. Aniline oligomers have been prepared and the different oxidation states studied by IR and UV measurements[316,317] as well as by X-ray analysis[317].

In the case of pyrrole oligomers both the approach of synthesizing a number of oligomers individually as well as the separation of a mixture of oligomers have been employed. The very elegant Stille coupling of N-Boc protected pyrroles by Martina et al. has afforded oligomers up to the nanomer. The crystal structures of the dimer[318], trimer[318] and pentamer[319] of this pyrrole series have been resolved. These clearly display a coplanar structure for the unprotected oligomers and a 70 degree angle for the N-Boc protected analogs. The Ullmann polymerization of 2,5-dibromo-N-Boc pyrrole has been used to produce a mixture of oligomers[104]. Subsequent HPLC separation affords all oligomers up to 20 repeating units. Doping of the pentamer has produced material with a conductivity of 100 Scm^{-1}.

Unsubstituted phenylene oligomers have been doped with potassium and the conductivity dependence of the chain length and structural order studied[320]. Some of the crystal structures were resolved[321]. Substituted phenylene oligomers have been doped and the formation of radical anions and dianions studied by optical measurements. These studies emphasize the influence of substituents on the aromatic backbone[322]. Acetylene oligomers are capped with t-butyl or phenyl groups to prevent side reaction during the studies. Oligomers containing two to four double bonds have been reduced and the different states studied with ESR (radical anions) and NMR (dianions)[323]. Oligomers containing up to 15 double bonds have been synthesized[324]. All-trans ß-carotene has been

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315 Thienpont, H.; Rikken, G. L. J. A.; Meijer, E. W.; ten Hoeve, W.; Wynberg, H. *Phys. Rev. Lett.* **1990**, *65*, 2141.

316 Lu, F.-L.; Wudl, F.; Nowak, M.; Heeger, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 8311.

317 Shacklette, L. W.; Wolf, J. F.; Gould, S.; Baughman, R. H. *J. Chem. Phys.* **1988**, *88*, 3955.

318 Street, G. B.; Lindsey, S. E.; Nazzal, A. I.; Wynne, K. *J. Mol. Cryst. Liq. Cryst.* **1985**, *118*, 137.

319 Martina, S.; Enkelmann, V.; Schlüter, A.-D.; Wegner, G.; Zotti, G.; Zerbi, G.; *Synth. Met.* **1993**, *55-57*, 1096.

320 Havinga, E. E,; Van Horssen, L. *Synth. Met.* **1987**, *17*, 623.

321 Baker, K. N.; Fratini, A. V.; Resch, T.; Knachel, H. C.; Adams, W. W.; Socci, E. P.; Farmer, B. L. *Polymer* **1993**, *34*, 1571.

322 Gregorius, H.; Heitz, W.; Müllen, K. *Adv. Mater.* **1993**, *5*, 279.

323 Schrenk, R.; Huber, W.; Schade, P.; Müllen, K. *Chem. Ber.* **1988**, *121*, 2201.

324 Knoll, K.; Schrock, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 7989.

used as an acetylene oligomer as well[325].

Substituted phenylene vinylene oligomers have been synthesized by a sequence of Wittig reactions[326] and their radical anion and dianions studied by optical methods[327]. Recently these oligomers have attracted considerable interest due to the electroluminescent properties of the parent polymer.

1.4 Aims of this thesis and survey of its contents

A considerable research effort has been devoted to the synthesis of π-conjugated materials with special emphasis on the solubility and purity of the materials as is illustrated in the previous sections. The introduction of side chains has proven to be effective for formation soluble polymers. Although these substituents provide solubility, they have a major influence on the characteristics of the materials, for example, the reduction of the effective conjugation length as a result of the steric interactions of the side chains. This is most pronounced for randomly attached substituents, but the effect is found in regioselectively substituted polymers as well. Furthermore, the regiorandom distribution also decreases the crystallinity. Therefore, a balance has to be found between solubility on the one hand and effective π-conjugation on the other. Although considerable research has been directed to the synthesis of either regioregularly substituted or partly substituted polythiophenes, a combination of both methodologies has not been examined yet. We expect that this combination, i.e. both a limited number and a regular attachment of substituents, will result in an increase in effective conjugation length. An important aspect of the purity of aromatic compounds is the question of π-conjugation through the aromatic backbone, i.e. the absence of mis-linkages that interrupt the conjugation. Especially, the widely used oxidative coupling of aromatic rings leaves some doubt about the coupling pattern of the rings. Additionally, with substituted monomers, oxidative methods may induce some side chain cross-linking. To prevent these unwanted side reactions, clean reactions are required. The best method for the direct coupling of aromatic rings is the organometallic cross-coupling reaction. Alternatively, heterocyclic rings can be synthesized by the cyclization of suitable precursor compounds, which in turn are prepared by well-

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325 Pellegrin, E.; Fritzsche, H.; Nücker, N.; Fink, J.; Drechsler, S. L.; Málek, J.; Meerholz, K.; Heinze, J.; Roth, S. *Synth. Met.* **1991**, *41-43*, 1207.

326 Schenk, R.; Gregorius, H.; Meerholz, K.; Heinze, J.; Müllen, K. *J. Am. Chem. Soc.* **1991**, *113*, 2635.

327 Schenk, R.; Gregorius, H.; Müllen, K. *Adv. Mater.* **1991**, *3*, 492.

defined methods. A combination of these two methods offers the possibility to synthesize π-conjugated compounds through a solid route that leaves no doubt about the perfect linkage of the aromatic rings. Furthermore, this allows the introduction of a variety of rings and substituents. In this thesis we will describe the design and synthesis of soluble oligomers and polymers with highly effective π-conjugation by using a limited number of substituents, sterically smaller substituents and a high degree of regioregularity of the substituents.

Chapter 2 deals with the synthesis of a highly conjugated and yet soluble polythiophene. The synthesis is based on the work of the group of McCullough, which uses a selectively prepared mono Grignard species, which is polymerized. We use a bithienyl derivative resulting in a polythiophene with one substituent on every two thiophene rings and with complete regioregularity of the substituents.

Chapter 3 describes the use of the Stetter reaction, i.e. the addition of cyanohydrin species to α,β-unsaturated ketones or precursor compounds thereof in the Michael reaction, for the synthesis of 1,4-diketones and the subsequent cyclization to afford thiophene and pyrrole derivatives. With this reaction several oligomers have been synthesized, containing different aromatic rings and various kinds of substituents. Additionally, the Stetter reaction and the ring-closure reactions are employed in the synthesis of aromatic polymers.

With the methods described above, highly conjugated materials have been obtained. However, the compounds are linear, and the effective conjugation length is dependent on the number of substituents and especially on the positioning of the substituents. An alternative strategy to increase the effective conjugation length is the synthesis of two dimensional compounds. This approach is described in chapter 4, where the pyrazine moiety is used as central building block for the synthesis of these types of molecules.

An important property of π-conjugated materials is their ability to conduct electric current upon doping. Most of the research on this topic has been carried out on the oxidized materials (p-type doping). n-Type doped conducting polymers have received far less attention although these materials are required for a number of applications. This limited attention is mainly due to instability of the materials that are obtained upon reduction of the virgin polymers. Alternatively, charge carriers may be introduced by the deprotonation of a suitable parent polymer. In chapter 5 we describe the synthesis of a 1,3-diketone polymer and its complexation with copper ions, in an attempt to prepare a stable n-doped conducting polymer.

Chapter two

Design and synthesis of regioregular poly(dodecyl-[2,2']-bithienyl)

2.1 Introduction

Polythiophenes can be made soluble by the introduction of appropriate alkyl substituents at the 3-position of the polymers. The introduction of these solubilizing side-chains, however, can have a negative effect on the conjugation length, due to steric interactions. Oxidative electrochemical polymerization as well as oxidative chemical polymerization gives rise to random coupling patterns with the substituents arranged head-to-head, head-to-tail and tail-to-tail. Generally, polythiophenes show 20% to 30% of the sterically unfavorable head-to-head couplings for the chemically[1] and the electro-chemically[2] prepared polymers, respectively. As a result of the coherency between the different couplings the same amount of tail-to-tail couplings are present as well. The tail-to-tail couplings cause no appreciable loss of conjugation. Irregularity as a whole, however, decreases the crystallinity of the materials. Polythiophenes prepared from 2,5-diiodothiophenes with magnesium and a nickel catalyst are, due to the isomeric mixture of Grignard species, regiorandom[3] as is the case in the polymers synthesized from 2,5-dihalothiophenes using zerovalent nickel complexes[4]. These head-to-head couplings can be avoided, either by the synthesis of a completely regioregular polythiophene or by the synthesis of a copolymer consisting of substituted and unsubstituted thiophene rings.

Regioregularity has been accomplished by using zinc instead of magnesium as metal, producing a monometallated monomer in a 9 : 1 ratio of the 2- and 5-metallated 3-alkylthiophene. The regularity of the corresponding polymer is completely dependent on the catalyst employed; a completely regiorandom polymer is obtained when $Pd(PPh_3)_4$ is used whereas $Ni(dppe)Cl_2$ produces a regioregularity of 98%[5]. The McCullough method, using a selectively prepared mono Grignard species, prepared in situ from the mono-lithium anion seems to be more general[6] (scheme 2.1). These perfect head-to-tail 2,5-linked polythiophenes exhibit enhanced properties versus regiorandom materials. Conduc-

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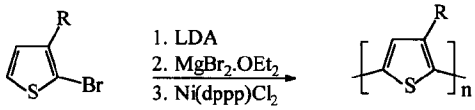
1 Leclerc, M.; Diaz, F. M.; Wegner, G. *Makromol. Chem.* **1989**, *190*, 3105
2 Sato, M.-a.; Morii, H. *Macromolecules* **1991**, *24*, 1196
3 Mao, H.; Zu, B.; Holdcroft, S. *Macromolecules* **1993**, *26*, 1163
4 Yamamoto, T.; Maruyama, T.; Zhou, Z.-H.; Miyazaki, Y. Kanbara, T.; Sanechika, K. *Synth. Met.* **1991**, 41-*43*, 345
5 Chen, T.-A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087
6 McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904

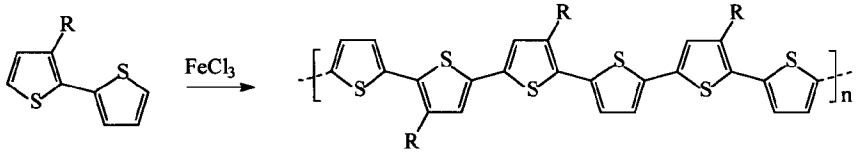
tivities up to 1000 Scm^{-1} and band gaps as low as 1.7 eV have been reported, whereas regiorandom polythiophenes have conductivities of 20 Scm^{-1} and band gaps in the order of 2.1 eV. Furthermore, regioregular polythiophenes display an increase in λ_{max} of 14 nm in solution up to 46 nm in the solid state.



scheme 2.1

The influence of the average number of alkyl substituents per thiophene unit on the effective conjugation length has been investigated in detail. Thiophene oligomers containing 11 thiophene rings with 3 alkyl side-chains (at rings 2, 6 and 10) and 12 thiophene rings with 4 alkyl side-chains (at rings 2, 5, 8 and 11) have been synthesized and studied[7,8]. These partly substituted thiophene oligomers show an increase in the λ_{max} of 20 to 30 nm compared with regiorandom poly(3-alkyl thiophene)s. For the synthesis of partly substituted polymers there are two possibilities: the use of monomers with one substituent on every two thiophene rings or the copolymerization of substituted and non-substituted monomers.

Monomers bearing one substituent on every two thiophene rings have been used in the polymerization. 3-Alkyl-[2,2']-bithienyls have been polymerized by oxidation with $FeCl_3$[9] and $Cu(ClO_4)_2$[10]. Although these polymers are not completely alternating, the substitution pattern inhibits all possible head-to-head couplings (scheme 2.2), and the absorption maximum is shifted 25 to 30 nm to longer wavelengths.



scheme 2.2

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7 a) ten Hoeve, W.; Wynberg, H; Havinga, E. E.; Meijer, E. W. *J. Am. Chem. Soc.* **1991**, *113*, 5887
b) Havinga, E. E.; Rotte, I.; Meijer, E. W.; ten Hoeve, W.; Wynberg, H. *Synth. Met.* **1991**, *41-43*, 473

8 Yasser, A.; Delabouglise, D.; Hmyene, M.; Nessak, B.; Horowitz, G.; Garnier, F. *Adv. Mater.* **1992**, *4*, 490.

9 Andersson, M. R.; Pei, Q.; Hjertberg, T.; Inganäs, O.; Wennerström, O.; Österholm, J.-E. *Synth. Met.* **1993**, *55-57*, 1227

10 Kaeriyama, K.; Masuda, H.; Shirakawa, H.; Akagai, K.; Suezawa, H.; Hirota, M. *Polym. Mater. Sci. Eng.* **1991**, *64*, 212

The copolymerization of substituted and unsubstituted thiophene monomers has received little attention in the literature, due to problems related to the structural features of the polymers as described in chapter one. Recently, however, McCullough et al. have used their method for the preparation of a copolymer of methyl and dodecyl substituted thiophenes[11]. Since preformed monomers are used in this polymerization, the coupling pattern is completely head-to-tail and the only irregularity present, is the homo coupling of methyl-substituted or dodecyl-substituted rings (figure 2.1). The polymer exhibits an increase in effective conjugation length relative to the regioregular all-dodecyl substituted polymer of 20 nm.

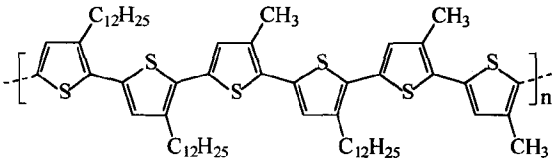
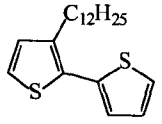
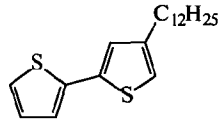


figure 2.1

In this chapter we will describe the synthesis of a soluble polythiophene with a high degree of coplanarity and crystallinity. To obtain a polymer exhibiting these characteristics, it is clear from the discussion above that a limited number of substituents and a high regularity in the positions of these substituents are required. Therefore, the target polymer should consist of completely alternating substituted and unsubstituted thiophene rings and the substituents must have an all-head-to-tail coupling pattern. We have chosen to prepare a mono-substituted bithienyl derivative and to polymerize it using the method developed by McCullough[6]. Consequently, the monomer should be a [2,2']-bithienyl derivative with the alkyl side chain in the 3- or 4-position, (compounds **2.1** and **2.2**) and introduce a bromine atom selectively in the 5- or 5'-position. Two approaches, starting with **2.1** and **2.2**, respectively, have been investigated and will be discussed. To obtain a good insight into the influence of the regioregularity, a regiorandom poly(3-dodecyl-[2,2']-bithienyl) has been synthesized as well, using a mild oxidative coupling reaction.



2.1



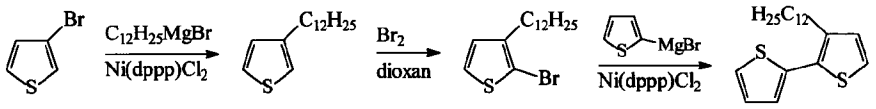
2.2

11 Jayaraman, M.; McCullough, R. D. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1994**, *35*, 299

2.2 Synthesis of regiorandom poly(3-dodecyl-[2,2']-bithienyl)

2.2.1 Monomer synthesis

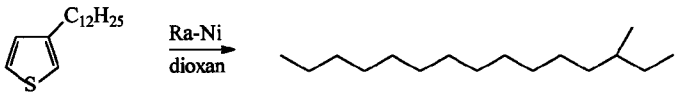
For the synthesis of alkyl-[2,2']-bithienyl derivatives several organometallic cross-coupling reactions have been described including the coupling of dodecylmagnesium bromide with 3-bromo-[2,2']-bithienyl[10] and the cross-coupling of 2-bromo-3-alkyl-thiophenes with 2-thienylboronic acid[9] or 2-thienylmagnesium bromide[12,13]. We have synthesized 3-dodecyl-[2,2']-bithienyl (**2.1**) via subsequent Grignard coupling reactions analogous to the literature procedures[12,13], as outlined in scheme 2.3.



2.3 2.4 2.5 2.1

scheme 2.3

Thus, 3-bromothiophene (**2.3**) and n-dodecylmagnesium bromide were coupled with $Ni(dppp)Cl_2$ as catalyst, to give **2.4** in a yield of 82% after distillation. Reduction of the product with Raney-nickel afforded 3-methylpentadecane (**2.6**), proving unambiguously that the product is 3-dodecylthiophene (**2.4**) (scheme 2.4).



2.4 2.6

scheme 2.4

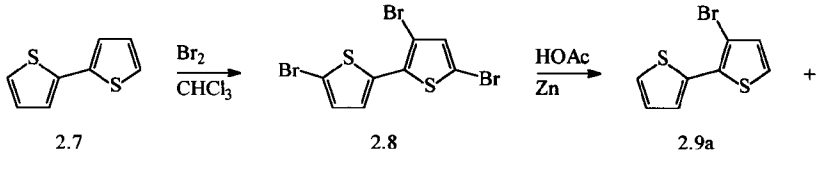
Bromination of **2.4** with bromine in dioxane[14] afforded 2-bromo-3-dodecylthiophene (**2.5**) in 90% yield. Coupling with 2-thienylmagnesium bromide gave 3-dodecyl-[2,2']-bithienyl (**2.1**) in 76% yield as a colorless oil (scheme 2.3). An alternative route to **2.1** that was investigated, is given in scheme 2.5. This method turned out to be less suitable due to the difficult preparation of **2.9a**. The key step in the synthesis of 3-bromo-[2,2']-bithienyl (**2.9a**), is the reductive debromination of 5,5',3-tribromo-[2,2']-bithienyl (**2.8**), synthesized

12 Van Pham, C.; Burkhardt, A.; Shabana, R.; Cunningham, D. D.; Mark jr., H. B.; Zimmer, H. *Phosphorus, Sulfur, and Silicon* **1989**, *46*, 153

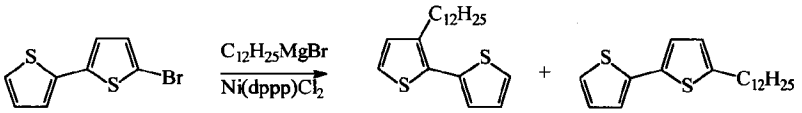
13 Bäuerle, P.; Pfau, F.; Schlupp, H.; Würthner, F.; Gaudle, K.-U.; Caro, M. B.; Fischer, P. *J. Chem. Soc., Perkin Trans. 2* **1993**, 489

14 Reinecke, M. G.; Adickes, H. W.; Pyun, C. *J. Org. Chem.* **1971**, *36*, 2690

by the bromination of [2,2']-bithienyl (**2.7**) with bromine in chloroform[15] analogous to the synthesis of tribromothiophene[16]. The reduction with zinc and acetic acid[17], however, yielded a mixture of monobromo compounds **2.9a** and **2.9b**. The ^{1}H-NMR spectrum of the alkylated products, obtained via the cross coupling, displayed for the methylene group attached to the thiophene ring two sets of absorptions, arising from isomer **2.1** and **2.10**.



2.7 2.8 2.9a

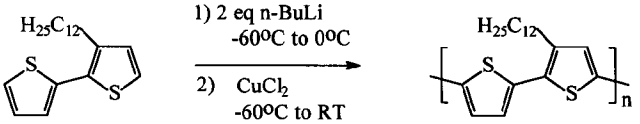


2.9b 2.1 2.10

scheme 2.5

2.2.2 Polymerization

Oxidative polymerization, as mentioned in chapter one, gives rise to side reactions. We therefore turned to the polymerization of the lithiated thiophene derivative with copper(II) chloride[18]. Thus, 3-dodecyl-[2,2']-bithienyl (**2.1**) was deprotonated with n-butyllithium and the resulting bis-anion polymerized with 2 equivalents of anhydrous copper(II) chloride at -60°C (scheme 2.6). The isolated solid was subjected to Soxhlet



2.1 2.11

scheme 2.6

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15 This method was used because of its relative simplicity compared to the reported bromination of 2,2'-bithienyl using $CuBr_2$ in CH_3CN. See Pyrka, G. J.; Fernando, Q.; Inoue, M. B.; Inoue, M. *Acta Cryst.* **1988**, *C44*, 1800

16 Troyanowsky, C. *Bull. Soc. Chim. Fr.* **1955**, 424

17 Gronowitz, S. *Acta Chem. Scand.* **1959**, *13*, 1045

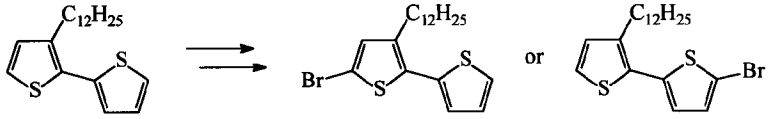
18 Kauffman, T. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 291

extraction with methanol and dichloromethane to remove impurities and low molecular weight fractions. Extraction with toluene afforded polymer **2.11** of high purity in 50% yield. The molecular weight of polymer **2.11** was determined by GPC with polystyrene standards and was estimated to be M_n = 9,600 g mol^{-1} with D=3.8. The polymer is insoluble in dichloromethane. This is at variance with the reported solubility in dichloromethane of poly(3-dodecyl-[2,2']-bithienyl) (**2.11**) synthesized by the oxidation of 3-dodecyl-[2,2']-bithienyl with copper(II) perchlorate[10].

2.3 Synthesis of regioregular poly(4-dodecyl-[2,2']-bithienyl)

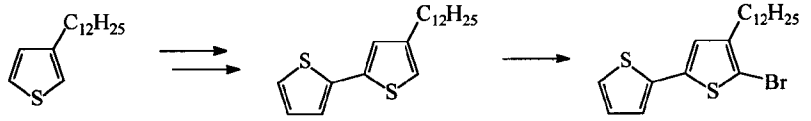
2.3.1 Monomer synthesis

For the synthesis of a regioregular poly(3-(or 4-)alkyl-[2,2']-bithienyl) using the McCullough method[6], the monomer should bear one bromine atom, positioned selectively at the 5- or 5'-position. We investigated two approaches for the synthesis of the monomer, starting with 3-dodecyl-[2,2']-bithienyl (**2.1**) and 4-dodecyl-[2,2']-bithienyl (**2.2**), respectively, as depicted schematically in figure 2.3. In both approaches, the bromine functionality has to be introduced specifically, since separation of the two isomers must be very difficult. 3-Alkylthiophenes can be brominated with complete selectivity at the 2-position. This selective bromination is the key step in both approaches. In the first approach it is used for the synthesis of 3-dodecyl-[2,2']-bithienyl (**2.1**) (see scheme 2.3). Since in compound **2.1** neither the 5-position nor the 5'-position is activated by the dodecyl substituent, the bromination, directly or indirectly, will be the difficult part. In the



2.1

Approach one



2.4 2.2

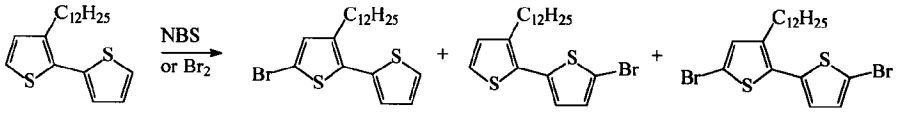
Approach two

figure 2.2 Regioregular poly(dodecyl-[2,2']-bithienyl); strategies for the monomer synthesis.

second approach, starting with 4-dodecyl-[2,2']-bithienyl (**2.2**), the 5-position is activated by the adjacent dodecyl group. Consequently, **2.2** can be brominated selectively at the 5-position, but in this case the synthesis of **2.2**, from 3-dodecylthiophene (**2.4**), will be the major hurdle. Both approaches will be discussed below.

2.3.1.1 First approach

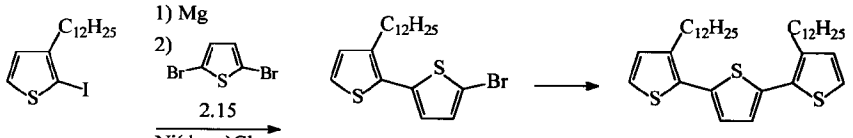
The most straightforward route for the synthesis of either 5- or 5'-bromo-3-dodecyl-[2,2']-bithienyl (**2.1**) is the direct bromination of **2.1** as outlined in scheme 2.7. Bromination of **2.1** with bromine or N-bromosuccimide (NBS) however, afforded a mixture of products including the bis-bromo **2.13** and both monobromo isomers **2.12a**, and **2.12b**. The only compound that could be isolated from the mixture with high purity was 5,5'-dibromo-3-dodecyl-[2,2']-bithienyl (**2.13**). Bäuerle et al.[13] reported the same phenomenon, although they observed a preference for bromination at the 5'-position (**2.12b**).



2.1 2.12a 2.12b 2.13

scheme 2.7

To avoid the necessity of brominating the bithienyl moiety, attempts were made to use 2,5-dibromothiophene (**2.15**) in the coupling reaction as outlined in scheme 2.8. The use of 2-bromo-3-dodecylthiophene (**2.5**) was unsuccessful due to the low reactivity of the bromide toward highly activated magnesium in ether. Therefore, the 2-iodo compound **2.14** was synthesized from 3-dodecylthiophene with mercury oxide and iodine[19], and used as synthesized with a purity of 85 %. It turned out, however, that even when an excess (approximately 1.8 equivalent) of dibromothiophene was used, the only isolated product



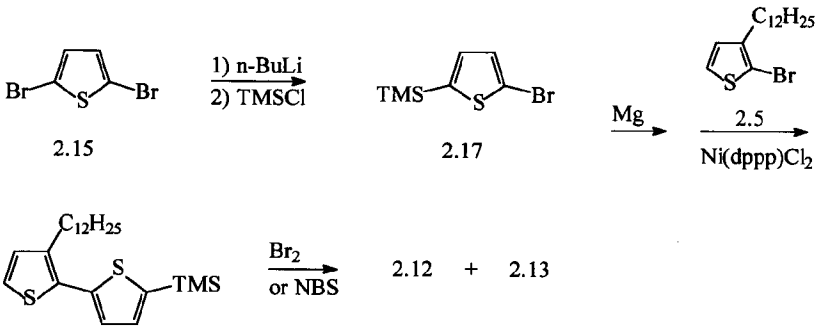
2.14 2.12b 2.16

scheme 2.8

19 Uhlenbroek, J. H.; Bijloo, J.D. *Rec. Trav. Chim. Pays-Bas* **1958**, *78*, 382

was the terthienyl derivative **2.16**[20] in a yield of 60%. This indicates that 3-dodecyl-5'-bromo-[2,2']-bithienyl (**2.12b**) has a higher reactivity than 2,5-dibromothiophene (**2.15**).

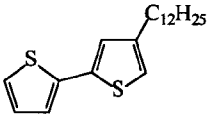
Protection of one α-position of **2.1** was accomplished as outlined in scheme 2.9. 2-Bromo-5-trimethylsilylthiophene (**2.17**) was synthesized by quenching the mono-lithium anion, prepared from 2,5-dibromothiophene (**2.15**) and one equivalent n-butyllithium, with trimethylsilyl chloride in ayield of 66%. The reaction with magnesium afforded the Grignard that was coupled with 2-bromo-3-dodecylthiophene (**2.5**) to give **2.18** in 84% yield. Bromination of the TMS substituted bithienyl compound **2.18**, however, yielded a reaction mixture similar to that obtained from the bromination of 3-dodecyl-[2,2']-bithienyl (**2.1**, scheme 2.5) containing **2.12** and **2.13**, both when NBS or bromine were used.



scheme 2.9

2.3.1.2 Second approach

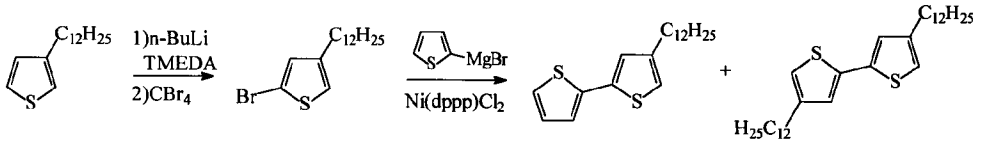
Since isolation of the 5- or 5'-bromo-3-dodecyl-[2,2']-bithienyl (**2.12a** or **2.12b**) proved very difficult, we directed our attention to the synthesis of 4-dodecyl-[2,2']-bithienyl (**2.2**), in order to utilize the higher reactivity of the α-position next to an alkyl substituent with respect to bromination as in 3-alkylthiophenes. Thus, 3-dodecylthiophene (**2.4**) was lithiated using a mixture of n-BuLi and TMEDA and the anion quenched with tetrabromometh-



2.2

20 The use of $PdCl_2$(1,1'-bis(diphenylphosphino)ferrocene) as catalyst in the cross-coupling of dibromobithienyl and thiophene magnesiumbromide has been reported to give the monobromo terthienyl, but again isolation was not possible. See reference 13

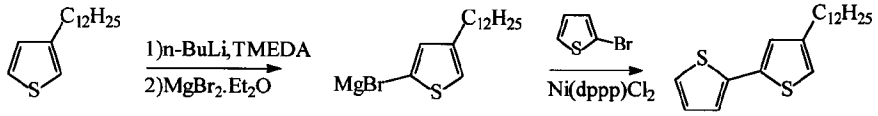
ane[21]. The obtained 2-bromo-4-dodecyl thiophene (**2.19**) contained 10 to 20% of the 2,3 isomer **2.5**. Crystallization from pentane at low temperatures increased the purity of **2.19** up to 95%. Coupling of **2.19** with 2-thienylmagnesium bromide and $Ni(dppp)Cl_2$ as catalyst in ether afforded **2.2** in 28% yield (scheme 2.10). These results are similar to the



2.4 2.19 2.2 2.20

scheme 2.10

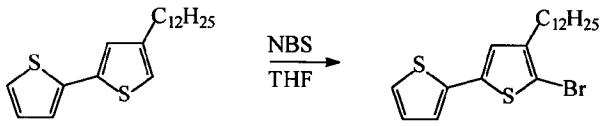
one reported for the methyl analog[13]. Increasing the reaction temperature by using THF as solvent, mainly induced the formation of the homo coupling product 4,4'-didodecyl-[2,2']-bithienyl (**2.20**). We therefore reversed the reaction pattern by preparing the Grignard reagent directly from the 4-dodecyl-2-lithiothiophene by quenching this with magnesium bromide and subsequent coupling with 2-bromothiophene as outlined in scheme 2.11. This



2.4 2.2

scheme 2.11

afforded 4-dodecyl-[2,2']-bithienyl (**2.2**) in 63% yield after crystallization from methanol-acetone. Bromination of **2.2** was realized with NBS in THF as outlined in scheme 2.12.



2.2 2.21

scheme 2.12

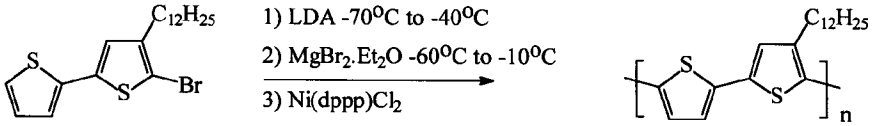
Although the use of bromine in dioxan afforded 2-bromo-3-dodecylthiophene (**2.5**) in high yields and high purity, NBS was used because the selectivity turned out to be equally high and NBS is easier to handle than bromine, specially on mmol scale reactions. An excess of

21 Consiglio,G.; Spinelli, D.; Gronowitz, S.; Hörnfeldt, A.-B.; Maltesson, B.; Noto, R. *J. Chem. Soc., Perkin Trans. 2* **1982**, 625

NBS would result in the formation of the 5,5'-dibromide. We expected that the presence of this by-product would hamper the purification of product **2.21** by crystallization, because the dibromide is expected to crystallize before product **2.21**. (This assumption was made based on the behavior of the 3-dodecyl-[2,2']-bithienyl derivatives **2.12** and **2.13**.) Therefore, 4-dodecyl-[2,2']-bithienyl (**2.2**) was used in an excess of 5%. Crystallization from methanol-acetone afforded 5-bromo-4-dodecyl-[2,2']-bithienyl (**2.21**) in 85% yield.

2.3.2 Polymerization

Polymerization was accomplished by means of the method developed by McCullough et al.[6] as depicted in scheme 2.13. Thus, 5-bromo-4-dodecyl-[2,2']-bithienyl (**2.21**) was deprotonated with lithium diisopropylamide at temperatures below -40°C, cooled to -60°C and the was anion quenched with magnesium bromide (freshly prepared from magnesium and dibromoethane in ether) affording the mono Grignard monobromide. At this stage the cooling bath was removed and at -10°C $Ni(dppp)Cl_2$ was added, the temperature allowed to reach room temperature and the reaction mixture was left overnight. The color of the reaction mixture changed from yellow to purple with increasing temperature. Quenching the reaction mixture with dilute hydrochloric acid afforded the crude polymer, which was subjected to Soxhlet extraction with methanol and dichloromethane to remove impurities and low molecular weight fractions. Extraction with THF afforded polymer **2.22** in 16% yield. The remainder consisted of higher molecular weight material, and an additional 1.5% yield could be obtained upon extractions with chlorobenzene.



2.21 2.22

scheme 2.13

During the reaction the color of the reaction mixture becomes purple, implying that the polymer has adopted an aggregated non-dissolved form, preventing further growth. The molecular weight, therefore, is not expected to be very high. An accurate molecular weight determination by GPC is not possible due to the aggregate conformation of the polymer at 20°C. GPC analysis is expected to display values far too high and would not provide reliable information about the molecular weight. ^{1}H-NMR at 110°C, to ensure a completely dissolved polymer, displays two distinct signals in the benzylic region. The signal with the highest intensity (at 2.70 ppm) is assigned to the benzylic protons of the

polymer chain, whereas the signal of lowest intensity (at 2.43 ppm) is thought to arise from the end-group benzylic moiety. Only the end-group with the dodecyl functionality directed away from the polymer chain will have an absorption at this position since this is the only side-chain that is not shielded by the thiophene backbone. End-group determination displays that compound **2.22** consists of approximately six monomeric units corresponding to an average molecular weight of 2000.

2.4 Absorption spectroscopy and thermochromism

The electronic absorption spectra of regiorandom poly(3-dodecyl-[2,2']-bithienyl) (**2.11**) and regioregular poly(4-dodecyl-[2,2']-bithienyl) (**2.22**) have been studied in solution in a temperature range from 20°C to 90°C. The maximum absorption of polymer **2.11** is found at 481 nm at 20°C. Polymer **2.11** displays a moderate thermochromic effect with an absorption shift, upon heating, of 15.2 nm from 481 nm to 465.8 nm (figure 2.3). Upon cooling, the original value of 481 nm is retrieved immediately, which indicates a very fast reversibility

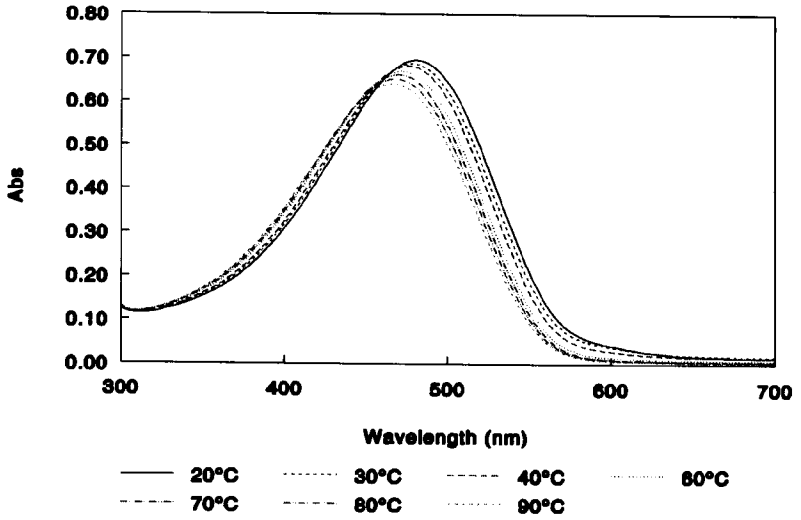


figure 2.3 *Absorption spectrum of polymer **2.11** upon heating (in di-chlorobenzene)*

The thermochromism of polymer **2.22** is considerably more pronounced. Upon heating, the absorption shifts from 530 nm to 466 nm with an isobestic point at 488 nm (figure 2.4). The absorption spectrum at 20°C clearly displays a second absorption

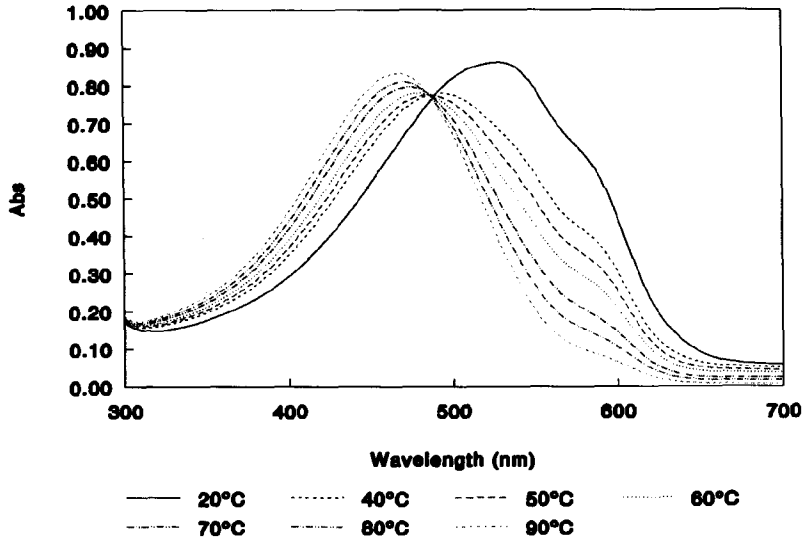


figure 2.4 Absorption spectrum of polymer 2.22 upon heating (in dichlorobenzene)

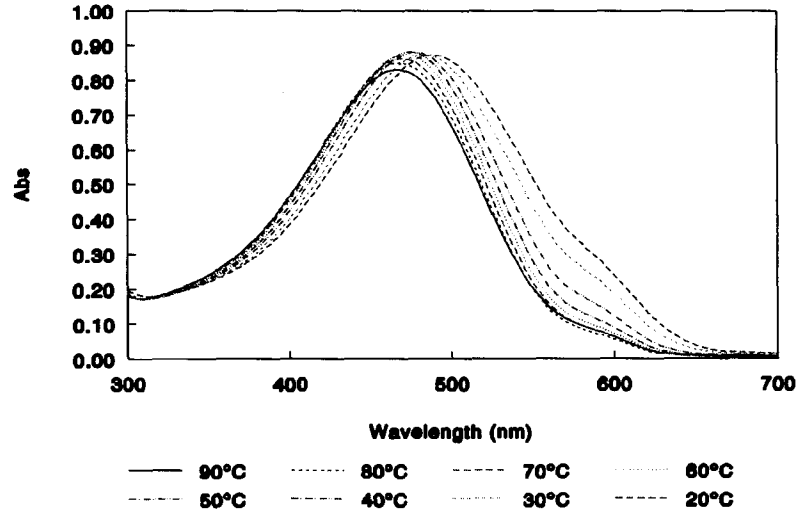


figure 2.5 Absorption spectrum of polymer 2.22 upon cooling (in dichlorobenzene)

maximum at 580 nm, indicative of the aggregated-form of the polymer at low temperatures as is seen in the solvatochromic effects of poly(3-alkylthiophene)s[22] as well as in their solid state spectra. Upon cooling, however, the absorption maximum shift is

22 Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1071

only 27.6 nm to 493 nm and the shape of the spectrum suggests that the polymer remains dissolved in a non-aggregated-form (figure 2.5). The aggregated-form (fig 2.4 20°C) is retrieved only after three days at 20°C, in contrast with the behavior of poly(3-dodecyl-[2,2']-bithienyl (**2.11**) and poly(alkylthiophene)s, which display a much more rapid reversibility.

2.5 Discussion

The synthesis of a suitable monomer for the preparation of a regioregular poly(dodecyl-[2,2']-bithienyl) has been accomplished starting with 4-dodecyl-[2,2']-bithienyl, using the activating influence of the n-dodecyl substituent. Bromination affords the 5-bromo derivative in high yield and high purity. The synthesis of 4-dodecyl-[2,2']-bithienyl via the preformed Grignard species of 3-dodecylthiophene has the advantage of a higher reactivity in the cross-coupling reaction. Moreover, using this route, the tedious preparation and purification of 2-bromo-4-dodecylthiophene becomes superfluous. Attempts to synthesize one of the two monobromo 3-dodecylbithienyl derivatives were unsuccessful. However, the fact that the coupling of 3-dodecyl-2-magnesium iodide with dibromothiophene affords the terthienyl derivative only implies that the reactivity in the Grignard coupling reaction increases with an increasing number of thiophene rings of the reactants. This is important when the reaction is applied to the synthesis of polymers, because it will result in polymer formation even when the overall conversion is lower than 90%. Bromination of the trimethyl silyl protected bithienyl derivative did not afford a single product when bromination was carried out with NBS or bromine, due to desilylation during the reaction. Trimethylsilyl groups are labile under acidic conditions, and HBr is present, either when bromine or NBS are used. Therefore, the introduction of the bromine atom should be carried out under neutral or alkaline conditions, and deprotonation and subsequent quenching with CBr_4 possibly would afford the mono brominated derivative. We have not investigated this possibility any further, since the synthesis of the monomer using the 4-dodecyl-bithienyl derivative turned out to be successful.

Polymerization using the McCullough route affords regioregular poly(dodecyl-[2,2']-bithienyl), emphasizing the general applicability of the method. The relative low isolated yield of the polymer is probably due to the fact that the conversion in the reaction is not very high, which is supported by the fact that some starting material was obtained by the methanol extraction, but also because polymer **2.22** is only partially soluble in THF. The molecular weight of polymer **2.22** is relatively low, arising mainly from the aggregation during the reaction but also from the low conversion. Although we have assigned the

resonance at 2.43 ppm to the benzylic end group, this is questionable, since signals arising from head-to-head couplings are found at the same frequency. If the signal arises from head-to-head couplings the average molecular weight would be much higher. The low solubility substantiates a high molecular weight. However, the rapid aggregation during the reaction and the well-resolved NMR signals do not coincide with a high molecular weight. Furthermore, head-to-head couplings would result in a polymer conformation with the dodecyl chains directed in both directions of the thiophene backbone. The large difference between polymer **2.11**, with the dodecyl group on both sides, and polymer **2.22** makes this highly unlikely. Therefore, we think that the signal at 2.43 ppm indeed arises from the end-groups.

Polymer **2.22** displays the expected enhanced conjugation length (an increase of 12 nm for the dissolved form of **2.22**), and a strong thermochromism. The remarkable slow aggregation of the polymer upon cooling is a result of the significant different structure of **2.22**, which has all the substituents on the same side of the thiophene backbone. There are two major differences between regioregular poly(3-dodecylthiophene) and polymer **2.22**; the number of substituents and the positioning of the substituents. Clearly, the number of substituents of polymer **2.22** accounts for the increase of 43 nm in effective conjugation length (λ_{max} of poly(3-dodecylthiophene) = 450 nm[6]). Poly(3-dodecylthiophene) has the substituents on both sides of the polymer backbone, enabling the polymer to adopt an aggregate structure very quickly (figure 2.6 a). Furthermore, this large, relatively lose structure is easily broken and solutions have to be cooled to -40°C to obtain a purple color. Polymer **2.22** on the other hand has the substituents attached on only one side of the aromatic backbone, assuming that it has an all-trans conformation.

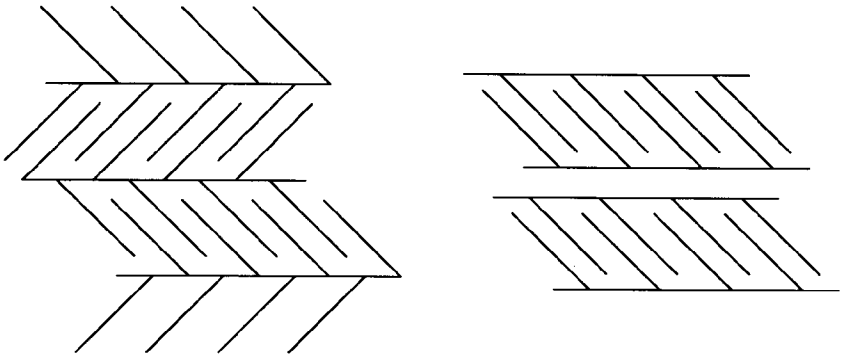


figure 2.6 *Schematic representations of the aggregated form of a) poly-(3-dodecyl thiophene) and b) poly-(4-dodecyl-[2,2']-bithienyl)*

Aggregation requires a pre-orientation of the polymer chains with the dodecyl moieties directed toward each other (figure 2.6 b). Therefore, the transition of the dissolved to the aggregated structure is very slow. A second consequence of the positioning of the substituents is that the aggregated form has a dimeric structure that is relative soluble and requires more energy to be broken. Consequently, solutions of polymer **2.22** are purple at room temperature. This aggregation behavior of polymer **2.22** is due to the positioning of the substituents and is not solely a result of the limited number of substituents, since the regiorandom polymer **2.11** displays a less pronounced thermochromism and a much faster reversibility.

For the synthesis of regiorandom poly(dodecyl-[2,2']-bithienyl) we have used 3-dodecyl-[2,2']-bithienyl, readily synthesized by the cross-coupling of 2-bromo-3-dodecylthiophene with thienylmagnesium bromide. The coupling reaction of 3-bromothiophene with dodecylmagnesium bromide affords 3-dodecylthiophene in high yields, but the product is contaminated with a few per cent tetracosane. Tetracosane is formed during the reaction either by homo-coupling of the Grignard species or by coupling of the Grignard species with dodecyl bromide, still present even when excess magnesium is employed. In the reaction, however, no bromine scrambling is observed that would result in the formation of 2-dodecylthiophene. The synthesis of 3-bromo-[2,2']-bithienyl via the zinc reduction of the tribromo derivative affords a mixture of bromides. This mixture arises from the difference in reactivity of the α-bromides due to the presence of only one bromine atom in a ß-position. This influence of adjacent bromine atoms has also been observed in the reduction of tetrabromo thiophene, which affords 3-bromothiophene when the same reaction conditions are employed as in the reduction of tribromo thiophene[16].

The low temperature oxidative polymerization of 3-dodecyl-[2,2']-bithienyl (**2.1**) produces a polymer with increased conjugation length compared with the polymer synthesized by the $Cu(ClO_4)_2$ oxidation of **2.1**[10] as shown by the room temperature absorption shift from 468 to 481 nm. An explanation for the difference in conjugation length of the two polymers must be found in the reaction conditions employed. The $CuCl_2$ polymerization is carried out at lower temperatures, uses a milder oxidant and preformed reaction sites. Deprotonation will occur at the α-positions, which are by far the most reactive as is the case in thiophene[23], and can be achieved using n-BuLi[24]. The use of n-BuLi diminishes possible side reactions such as complexation of copper chloride with

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23 Wynberg, H.; Bantjes, A. *J. Am. Chem. Soc.* **1960**, *82*, 1447

24 Berlin, A.; Pagani, G. A.; Sannicolò, F. *J. Chem. Soc., Chem. Commun.* **1986**, 1663

TMEDA or coupling reactions with butyl bromide. These side reaction may occur using methods described for the formation of dilithio-thiophenes[25]: n-BuLi and TMEDA[26] or halogen lithium exchange reactions with dibromo thiophene and butyllithium[27]. The results substantiate the literature observations[28] that oxidative polymerizations give rise to considerable cross-linking of the alkyl side chains. Intramolecular cross-linking of the side chains results in a bended molecule with decreased planarity. Intermolecular cross-linking increases the observed molecular weight, although the conjugated segments are relatively small. In both instances, the structural order of the polymer is limited. The molecular weight of the polymers prepared by the $FeCl_3$ and the $Cu(ClO_4)_2$ oxidations of **2.1** and polymer **2.11** are roughly the same. Consequently, the conjugated segments of **2.11** are more planar and larger. Furthermore, polymer **2.11** has a higher structural order and this, together with the increased conjugation length accounts for the decreased solubility.

2.6 Concluding remarks

In this chapter we have described the synthesis of poly(dodecyl-[2,2']-bithienyl)s, both regiorandom and regioregular. Evidently the low temperature oxidative polymerization of 3-dodecyl-[2,2']-bithienyl has led to a polymer with an increased effective conjugation length. Regioregularity was accomplished using 4-dodecyl-[2,2']-bithienyl via the preformed mono-Grignard species, and the polymer displays the expected enhanced conjugation length, and a remarkable thermochromism. Improving the structural regularity however, has a negative effect on the solubility emphasizing the delicate balance between solubility on one hand and high conjugation length and structural order on the other.

2.7 Experimental section

General remarks

Melting points were determined on a Mettler FP-2 melting point apparatus, equiped with a Mettler FP-21 Microscope. ^{1}H-NMR spectra were recorded on a Varian Geminin-200 (200 MHz) or on a Varian VXR-300 (300 MHz). Chemical shifts are denoted in δ-units (ppm) relative to the solvent and converted to the TMS scale using δ ($CHCl_3$) = 7.26 ppm, δ (H_2O) = 4.65 ppm and δ (DMSO) = 2.49 ^{13}C-NMR were recorded on a Varian Gemini-200 (at 50.32 MHz) or on a Varian VXR-300 (at 75.48 MHz). Chemical shifts are denoted in

25 The use of lithium diisopropylamide as lithiating agens gives high yields in the coupling reaction as well, see: Kagan, J.; Arora, S. K. *Heterocycles* **1983**, *20*, 1937

26 Feringa, B. L.; Hulst, R.; Rikers, R.; Brandsma, L. *Synthesis* **1988**, 316

27 Amer, A.; Zimmer, H.; Mulligan, K. J.; Mark jr., H. B.; Pons, S.; McAleer, J. F. *J. Pol. Sci.: Polym. Lett. Ed.* **1984**, *22*, 77

28 Gautun, O. R.; Carlsen, P. H. J.; Samuelsen, E. J.; Mårdalen, J. *Synth. Met.* **1993**, *58*, 115.

δ-units (ppm) relative to the solvent and converted to the TMS scale using δ ($CHCl_3$) = 76.9 ppm in the APT mode. The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and b (broad). Coupling constants are given in Herz. Elemental analysis were performed in the microanalytical department of this laboratory by Mr H. Draayer, J Ebels, J.Hommes and J. E. Vos. Mass spectra were recorded on an AET-MS-902 mass spectrometer by Mr A Kiewiet. UV spectra were recorded on a Perkin-Elmer Lambda 3b UV/VIS spectrophotometer by Mr M. M. Bouman, University of Technology, Eindhoven.

All solvents were distilled, when necessary, prior to use. DMF was stored on 4 Å sieves and THF was distilled from Na wire. 2-bromothiophene, 3-bromothiophene (**2.3**), n-dodecylbromide, 2,5-dibromothiophene (**2.15**), and CBr_4 were purchased from Janssen Chimica and used a received. Ni(dppp)Cl_2 was purchased from Aldrich. Tetramethylethylenediamine (TMEDA, Janssen) was stored on KOH pellets and $CuCl_2$ was dried at 120°C.All reactions were carried out under a nitrogen atmosphere when necessary.

3-Dodecylthiophene (2.4)[29]

A solution of dodecyl bromide (95 g, 380 mmol) in ether (300 ml) was added to Mg (9.3 g, 385 mmol) over 1.5 h maintaining a gentle reflux. The Grignard solution was added to a mixture of 3-bromothiophene (**2.3**) (50 g, 306 mmol) and 250 mg Ni(dppp)Cl_2 in ether (500 ml) at 0°C in 1 h. The mixture was allowed to warm up and after the spontaneous reflux had subsided the reaction mixture was refluxed for another 6 hours. After cooling to 0°C it was hydrolysed with 2N HCl (300 ml). The layers were separated and the aqueous layer extracted with ether (2x200 ml). The combined organic layers were washed with water, a $NaHCO_3$ solution, water, brine and dried (Na_2SO_4). The ether was evaporated and the residue distilled giving 64 g (82%) of **2.4** as a colorless oil. (b.p. 110-130°C, 0.03-0.05 mbar). ^{1}H-NMR ($CDCl_3$) δ:0.94 (t, 3H), 1.36 (m, 18H), 1.67 (m, 2H), 2.67 (t, 2H), 6.96 (m, 2H), 7.27 (dd, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:14.0 (q), 22.6 (t), 29.3 (t), 29.4 (t), 29.6 (t), 30.2 (t), 30.5 (t), 31.8 (t), 119.6 (d), 124.9 (d), 128.2 (d), 143.1 (s) ppm.

3-Methylpentadecane (2.6)

Raney-nickel was prepared according to a literature procedure[30] from Ni-Al alloy (15 g) and NaOH (19 g) in H_2O (75 ml). To the anhydrous Raney-nickel was added dioxane (100 ml) and 3-dodecylthiophene (**2.4**) (0.5 g). The reaction mixture was refluxed for 16 h, filtered and washed with ether. The solvents were evaporated and the residue distilled (kugelrohr) giving 0.35 g of **2.6** as a colorless oil. ^{1}H-NMR ($CDCl_3$) δ:0.88 (m, 9H), 1.28 (m, 25H) ppm. ^{13}C-NMR ($CDCl_3$) δ:11.3 (q), 14.0 (q), 19.2 (q), 22,7 (t), 27.1 (t), 29.0 (t), 29.4 (t), 29.5 (t), 29.7 (t), 30.1 (t), 31.9 (t), 34.4 (d), 36,6 (t) ppm. MS m/e: 226 (M^+), 197 (46%, -Et), 57 (100%, Bu).

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29 Sato, M.-a; Tanaka, S.; Kaeriyama, K. *Makromol. Chem.* **1987**, *188*, 1763

30 Vogel, A. I. *Textbook of practical organic chemistry* 4th Ed., Longman Inc. New York **1978** p 303

2-Bromo-3-dodecylthiophene (2.5)[6,13]

The compound was synthesized in analogy with a literature procedure[14]. To a solution of 3-dodecylthiophene (**2.4**) (33.5 g, 133 mmol) in dioxane (300 ml) was added Br_2 (21.2 g, 133 mmol) in dioxane (450 ml) in 1.5 h The reaction mixture was poured in 700 ml of a $NaHCO_3$ solution and extracted with hexane (3x250 ml). The organic layer was washed with brine and dried. (Na_2SO_4) Evaporation of the solvent and distillation (kugelrohr) gave 39.8 g (90%) of **2.5** as a slightly colored oil. (b.p. 165°C, 0.05 mbar). ^{1}H-NMR ($CDCl_3$) δ:0.89 (t, 3H), 1.28 (m, 18H), 1.58 (m, 2H), 2.57 (t, 2H), 6.80 (d, J=5.6 Hz, 1H), 7.18 (d, J=5.6 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:14.0 (q), 22.6 (t), 29.1 (t), 29.3 (t), 29.5 (t), 29.6 (t), 31.8 (t), 108.7 (s), 125.0 (d), 128.1 (d), 141.9 (s) ppm. HRMS calcd. for $C_{16}H_{27}BrS$: 330.102, found: 330.102.

3-Dodecyl-[2,2']-bithienyl (2.1)[13]

A solution of 2-thienylmagnesium bromide (prepared from 2-bromothiophene (13.8 g, 85 mmol) and Mg (2.1 g, 86 mmol) in ether (150 ml)) was added to a solution of 19.4 g (59 mmol) 2-bromo-3-dodecylthiophene (**2.5**) and 50 mg Ni(dppp)Cl_2 in 200 ml ether at 0°C. The mixture was left at RT overnight, refluxed for 7 h and hydrolysed with 2N HCl (75 ml). The layers were separated and the aqueous layer extracted with ether (2x100 ml). The combined organic layers were washed with a $NaHCO_3$ solution, water and brine and dried (Na_2SO_4). The solvent was evaporated and the residue distilled (kugelrohr) giving 15.4 g (76%) of **2.1** as a slightly colored oil.(b.p. 200°C, 0.05 mbar) ^{1}H-NMR ($CDCl_3$) δ:0.93 (t, 3H), 1.30 (m, 18H), 1.63 (m, 2H), 2.78 (t, 2H), 6.96 (d, 1H), 7.06-7.20 (m, 3H), 7.32 (d, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:14.1 (q), 22.6 (t), 29.0 (t), 29.3 (t), 29.4 (t), 29.6 (t), 30.6 (t), 31.8 (t), 123.5, (d), 125.1 (d), 125.8 (d), 127.2 (d), 129.7 (d), 130.4 (s), 136.2 (s), 139.5 (s) ppm. anal. calcd. for $C_{20}H_{30}S_2$: C 71.80, H 9.04, S 19.17, found: C 71.79, H 9.00, S 18.91.

3,5,5'-Tribromo-[2,2']-bithienyl (2.8)[31]

To a mixture of [2,2']-bithienyl (**2.7**) (7.67 g, 46 mmol) in $CHCl_3$ (50 ml) cooled by means of an ice-bath, was added bromine (22.15 g, 138 mmol) in $CHCl_3$ (50 ml). The reaction mixture was allowed to reach RT and washed with water, a $NaHCO_3$ solution, brine and dried (Na_2SO_4). Evaporation of the solvent and recrystallization from ethanol afforded 12.7 g (69%) of **2.8** as a yellow solid. mp: 84.4-85.7 °C. ^{1}H-NMR ($CDCl_3$) δ:6.96 (s, 1H), 7.02 (dd, 2H) ppm. ^{13}C-NMR ($CDCl_3$) δ:107.1 (s), 111.4 (s), 113.6 (s), 126.9 (d), 129.9 (d), 133.0 (s), 133.7 (d), 134.6 (s) ppm.

Attempted synthesis of **3-Dodecyl-[2,2']-bithienyl (2.1)**

A mixture of **2.8** (1 g, 2.5 mmol), HOAc (0.5 ml), water (1.5 ml), Zn (0.95 g) and n-PrOH (10 ml) was refluxed for 18 h. The solvents were evaporated, ether and diluted HCl were added, and the layers separated.

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31 Although the compound has been used, the authors give no other experimental data apart from the X-ray structure. See Pyrka, G. J.; Fernando, Q.; Inoue, M. B.; Inoue, M. *Acta Cryst.* **1988**, *C44*, 1800

The organic layer was washed with a $NaHCO_3$ solution, brine and dried (Na_2SO_4). Evaporation of ether and distillation afforded 400 mg of **2.9** as a slightly colored oil. Coupling of **2.9** with dodecyl magnesium bromide afforded both 2- and 5-dodecyl-[2,2']-bithienyl (**2.1** and **2.10** respectively) (^{1}H-NMR resonances of the benzylic protons of **2.10** are found at 2.61 ppm.

Poly-(3-dodecyl-[2,2']-bithienyl) (2.11)

A solution of **2.1** (1.02 g, 3 mmol) in THF (30 ml) was cooled to -70°C, n-BuLi (1.6 M, 4 ml) was added and the temperature allowed to reach 0°C resulting in a suspension. This suspension was kept at 0°C for 1,5 h, recooled to -70°C and $CuCl_2$ (900 mg, 6.7 mmol, dried at 120°C) was added. The temperature was allowed to reach RT during what time the color changed to black. The mixture was poured in water (300 ml) and HCl (25 ml,conc) and the dark solid collected and transferred to a soxlet apparatus. It was extracted with MeOH for 16 h, with CH_2Cl_2 for 20 h and finally with toluene for 16 h. The toluene was evaporated to afford 500 mg of **2.11** as a purple solid with a green metallic luster. anal. calcd. for $(C_{20}H_{28}S_2)_n$: C 72.23, H 8.49, S 19.28, found: C 71.40, H 8.56, S 18.88.

Attempted synthesis of **3-dodecyl-5-bromo-[2,2']-bithienyl (2.12a)** or **3-dodecyl-5'-bromo-[2,2']-bithienyl (2.12b)**

To a solution of 3-dodecyl-[2,2']-bithienyl (**2.1**) (1 g, 3 mmol) in dioxane (10 ml) was added Br_2 (540 mg, 3mmol) in dioxane (5 ml). The mixture was stirred for 1 h at RT, poured in water (50 ml) and extracted with ether (3x40 ml). The organic layers were washed with water, brine, dried (Na_2SO_4) and the solvents evaporated. ^{1}H-NMR of the crude material clearly showed the existence of a mixture of bromides **2.12** and **2.13**, probably also containing some starting material. Crystallization from pentane afforded 3-dodecyl-5,5'-dibromo-[2,2']-bithienyl (**2.12**) as white crystals. ^{1}H-NMR ($CDCl_3$) δ:0.90 (t, 3H), 1.27 (m, 18H), 1.58 (m, 2H), 2.64 (t, 2H), 6.80 (d, J=3.8 Hz, 1H), 6.89 (s, 1H), 7.00 (d, J=3.8 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:14.0 (q), 22.6 (t), 28.9 (t), 29.3 (t), 29.4 (t), 29.6 (t), 30.5 (t), 31.8 (t), 110.9 (s), 112.3 (s), 126.5 (d), 130.1 (d), 130.8 (s), 132.4 (d), 136.2 (s), 140.7 (s) ppm.

Attempted synthesis of **3-dodecyl-5'-bromo-[2,2']-bithienyl (2.12b)**

A solution of 3-dodecylthiophene (**2.4**) (3 g, 11.9 mmol) in toluene (20 ml) was cooled by means of a water bath and HgO (2.4 g, 11 mmol) and I_2 (3.1 g, 12 mmol) were added in small portions. Ether (50 ml) was added and the mixture filtered, washed with water and dried (Na_2SO_4). Evaporation of the solvents yielded 2-iodo-3-dodecyl thiophene (**2.15**) (3 g) with a purity of 85% (according to ^{1}H-NMR (60 MHz)). This was dissolved in ether (30 ml) and added to activated Mg (200 mg). The resulting Grignard reagent was added to 2,5-dibromothiophene (3 g, 12mmol) and a catalytic amount Ni(dppp)Cl_2 in ether (40 ml). After stirring at RT overnight and reflux for 7 h the mixture was hydrolysed with diluted HCl. The aqueous phase was extracted with ether, the combined organic layers were washed with water, brine and dried (Na_2SO_4). Evaporation of the solvent and excess **2.15** and chromatography (silicagel, pentane) afforded 1.2 g of 3-3''-didodecyl-2,2,5',2''-terthienyl (**2.16**). ^{1}H-NMR ($CDCl_3$) δ:0.90 (t, 6H), 1.27 (m, 36H), 1.67 (m, 4H), 2.80 (t, 4H), 6.95 (d, J=5.1 Hz, 2H), 7.07 (s, 2H), 7.18 (d, J=5.1 Hz, 2H) ppm. ^{13}C-NMR ($CDCl_3$) δ:14.0 (q), 22.6

(t), 29.2 (t), 29.2 (t), 29.4 (t), 29.5 (t), 29.6 (t), 30.6 (t), 31.8 (t), 123.6 (d), 125.9 (d), 129.9 (d), 130.3 (s), 135.9 (s), 139.5 (s) ppm.

2-Bromo-5-trimethylsilylthiophene (2.17)

To a cooled solution of 2,5-dibromothiophene (**2.15**) (23.4 g, 97 mmol) in THF (100 ml) was added n-BuLi (1.6M, 64 ml) at such a rate that the temperature maintained below -65°C. After 0.5 h at this temperature TMSCl (13 ml) was added, the reaction mixture allowed to reach 5°C and hydrolyzed with NH_4Cl. The layers were separated, the aqueous phase extracted with hexane (3x100 ml), the combined organic layers washed with water, brine and dried (Na_2SO_4). Distillation (kugelrohr 120°C 20 mm Hg) afforded 15 g (66%) of **2.17**. ^{1}H-NMR ($CDCl_3$) δ:0.32 (s, 9H), 7.00 (d, J=3.4 Hz, 1H), 7.09 (d, J=3.4 Hz, 1H) ppm.

3-Dodecyl-5'-(trimethylsilyl)-[2,2']-bithienyl (2.18)

A solution of 2-bromo-5-trimethylsilylthiophene (**2.17**) (4.8 g, 20.5 mmol) in ether (30 ml) was added to activated Mg (500 mg, 20.8 mmol). The resulting Grignard reagent was added to **2.5** (4.95 g, 15 mmol) and Ni(dppp)Cl_2 (200 mg) in ether (50 ml) and the mixture refluxed for 6h. The reaction mixture was hydrolyzed with water, the organic phase washed with brine and dried (Na_2SO_4). Evaporation and distillation (kugelrohr 200°C 0.05 mbar) afforded 5.1 g (84%) of **2.18**. ^{1}H-NMR ($CDCl_3$) δ:0.36 (s, 9H), 0.90 (t, 3H), 1.29 (m, 18H), 1.65 (m, 2H), 2.78 (t, 2H), 6.94 (d, 1H), 7.18 (m, 3H) ppm. ^{13}C-NMR ($CDCl_3$) δ:-0.2 (q), 14.0 (q), 22.6 (t), 28.7 (t), 29.1 (t), 29.3 (t), 29.4 (t), 29.4(t), 29.6 (t), 30.6 (t), 31.8 (t), 123.5 (d), 126.9 (d), 129.8 (d), 130.6 (s), 134.1 (d), 139.3 (s), 141.4 (s) ppm.

2-Bromo-4-dodecylthiophene (2.19)

To a solution of 3-dodecylthiophene (**2.4**) (12.8 g, 50.8 mmol) in ether (70 ml) was added a mixture of n-BuLi (1.5M, 34 ml) and TMEDA (8 ml, 53 mmol) and mechanically stirred at RT for 1 h. After cooling to -65°C CBr_4 (14 g) in ether (50 ml) was added and the suspension stirred at the same temperature overnight. The dark mixture was allowed to reach -10°C and poured in diluted HCl. The aqueous phase was extracted with ether (3x75 ml), the combined organic layers washed with water and dried (Na_2SO_4). Evaporation of the solvent and distillation (kugelrohr, 170°C 0.05 mbar) afforded 12.2 g (72%) of **2.19** containing 20% of **2.5**. Further purification was accomplished by crystallization from pentane at -25°C affording almost pure **2.19** as an oil. ^{1}H-NMR ($CDCl_3$) δ:0.91 (t, 3H), 1.29 (m, 18H), 1.59 (m, 2H), 2.56 (t, 2H), 6.81 (d, J=1.7 Hz, 1H), 6.89 (d, J=1.7 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:14.0 (q), 22.6 (t), 29.1 (t), 29.2 (t), 29.3 (t), 29.5 (t), 29.6 (t), 30.1 (t), 30.5 (t), 31.8 (t), 111.5 (s), 121.2 (d), 130.8 (d), 143.7 (s) ppm. HRMS calcd. for $C_{16}H_{27}BrS$: 330.102, found: 330.102.

4-Dodecyl-[2,2']-bithienyl (2.2)

a) from **2.19**

2-Thienylmagnesium bromide (70 mmol) in ether (50 ml) was added to **2.19** (12 g, 36 mmol, 80% pure) and Ni(dppp)Cl_2 (300 mg) in THF (100 ml). The mixture was refluxed for 6 days and hydrolysed with diluted HCl. The aqueous phase was extracted with ether (3x100 ml), the organic layers washed with water, brine,

dried (Na_2SO_4), and the solvent evaporated. Distillation (kugelrohr 150°C to 200°C 0.05 mbar) and crystallization from MeOH acetone (1:1) afforded 2.95 g (28%) of **2.2**. The residue consisted of 4,4'-didodecyl-[2,2']bithienyl (**2.20**). ^{1}H-NMR ($CDCl_3$) δ:0.90 (t, 6H), 1.31 (m, 36H), 1.63 (m, 4H), 2.58 (t, 4H), 6.77 (s, 2H), 6.98 (s, 2H) ppm. ^{13}C-NMR ($CDCl_3$) δ:14.0 (t), 22.6 (t), 29.2 (t), 29.4 (t), 29.6 (t), 30.3 (t), 30.4 (t), 31.8 (t), 118.5 (d), 124.7 (d), 143.8 (s) ppm. HRMS calcd. for $C_{32}H_{54}S_2$: 502.067, found: 502.067.

b) from **2.4**

To a solution of 3-dodecylthiophene (**2.4**) (10.45 g, 41.5 mmol) in ether (75 ml) was added dropwise a mixture of n-BuLi (1.6M, 26 ml) and TMEDA (6.25 ml, 41.6 mmol) at RT and stirred for 1 h. The suspension was cooled to -50°C and $MgBr_2$ (43 mmol, freshly prepared from dibromoethane (7.9 g) and Mg (1.1 g) in ether (20 ml)) was added. The temperature was allowed to rise to -25°C resulting in a almost clear solution, turning cloudy again after a further increase of the temperature. At -20°C 2-bromothiophene 10 g, 61 mmol) and Ni(dppp)Cl_2 (50 mg) were added. The reaction mixture was refluxed for 70 h during what time it was concentrated to half its original volume. The dark mixture was poured in cold 2N HCl and extracted with ether (3x100 ml). The organic layers were washed with water, a $NaHCO_3$ solution, brine and dried (Na_2SO_4). Evaporation of the solvents and distillation of the residue (kugelrohr) afforded an oil (bp 170-190°C 0.005-0.01 mbar), also containing a few per cent of the 3-isomer (**2.1**). Crystallization from MeOH-acetone (1:1) gave 8.75 g (63%) of **2.2** as a white solid. mp: 32.2-33.1°C. ^{1}H-NMR ($CDCl_3$) δ:0.90 (t, 3H), 1.27 (m, 18H), 1.55 (m, 2H), 2.58 (t, 2H), 7.79 (d, J=1.3 Hz, 1H) 7.0 (m, 2H), 7.14 (dd, J=3.8 Hz, J=1.3 Hz, 1H), 7.19 (dd, J=5.1 Hz, J=1.3 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:14.0 (q), 22.6 (t), 29.2 (t), 29.4 (t), 29.6 (t), 30.3 (t), 30.4 (t), 31.8 (t), 118.8 (d), 123.3 (d), 123.9 (d), 125.0 (d), 127.6 (d), 136.8 (s) 137.7 (s), 143.9 (s) ppm. anal. calcd. for $C_{20}H_{30}S_2$: C 71.80, H 9.04, S 19.17, found: C 71.98, H 9.17, S 18.72. HRMS calcd. for $C_{20}H_{30}S_2$: 334.179, found: 334.179.

5-Bromo-4-dodecyl-[2,2']-bithienyl (2.21)

To a cold solution of 4-dodecyl-[2,2']-bithienyl (**2.2**) (7.54 g, 22.6 mmol) in THF (75 ml) was added NBS (3.8 g, 21.5 mmol). The mixture was stirred overnight, slowly reaching RT, poured into a $NaHCO_3$ solution and extracted with ether (3x75 ml). The combined organic layers were washed with water, brine and dried (Na_2SO_4). The solvent was evaporated and the residue crystallized from MeOH-acetone (1:1). This gave 7.9 g (85%) of **2.21** as a white solid. mp: 27.6-29.6°C. ^{1}H-NMR ($CDCl_3$) δ:0.90 (t, 3H), 1.28 (m,18), 1.60 (m, 2H), 2.54 (t, 2H), 6.87 (s, 1H), 7.00 (dd, J=5.1 Hz, J=3.9 Hz, 1H), 7.10 (dd, J=3.9 Hz, J=1.3 Hz, 1H), 7.21 (dd, J=5.1 Hz, J=1.3 Hz, 1H) ppm.^{13}C-NMR ($CDCl_3$) δ:14.0 (q), 22.6 (t), 29.1 (t), 29.3 (t), 29.5 (t), 29.6 (t), 31.8 (t), 107.4 (s), 123.5 (d), 124.4 (d), 127.7 (d), 136.7 (s), 142.7 (s) ppm. anal. calcd. for $C_{20}H_{29}BrS_2$: C 58.10, H 7.07, Br 19.32, S 15.51, found: C 58.02, H 7.01, Br 19.04, S 15.33. HRMS calcd. for $C_{20}H_{29}BrS_2$: 412.089, found: 412.089.

Poly-5,5'-(4-dodecyl-[2,2']-bithienyl) (2.22)

To a solution of LDA (8 mmol, prepared from n-BuLi (1.6 N, 5 ml) and diisopropylamine (1.12 ml)) in THF (75 ml) at -70°C was added a solution of 5-bromo-4-dodecyl-[2,2']-bithienyl (3 g, 7.3 mmol) in THF (8 ml). The solution was kept between -50 and -40°C for 40 min, recooled to -70°C and $MgBr_2$ (9 mmol,

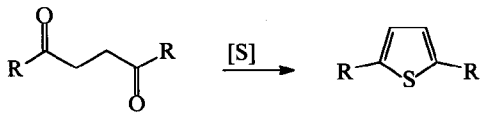
freshly prepared from dibromoethane (1.7 g) and Mg (250 mg) in ether (20 ml)) was added. The cooling bath was removed and at a temperature of -8°C Ni(dppp)Cl_2 (50 mg) was added. The mixture was stirred for 20 h reaching RT, the color changing from yellow to dark red/purple. It was poured into MeOH-water (700 ml 1:1), the solid collected and washed with water. The crude polymer was subjected to soxlet extraction with MeOH (16 h), affording also a little amount of **2.21**, and CH_2Cl_2 (18 h) to remove impurities and low molecular weight material. Upon extraction with THF for 16 h 390 mg (16%) of the polymer was isolated as a purple material. The remainder was extracted with chlorobenzene to afford another 37 mg (1.5%). Further extraction with dichlorobenzene yielded some additional polymer, but the solvent induced some degradation. ^{1}H-NMR (C_6D_5Br, 110°C) δ:0.77 (m, 3H); 1.19 (m, 16H); 1.33 (m, 2H); 1.60 and 1.63 (2 x m, 2H) 2.43 (m, 0.35H), 2.70 (m, 1.65H), 6.94 (m, 3H) ppm.

Chapter three

Synthesis of well-defined oligomers and polymers containing thiophene, phenylene and pyrrole moieties using the Stetter reaction.

3.1 Introduction

Oligomers can be used to assess conformational and optical features of π-conjugated polymers. Additionally, they can serve as monomers. To be useful models, oligomers must be structurally well-defined and consequently, unambigious reactions are required for their synthesis. For the synthesis of α-thiophene oligomers a number of methods have been developed[1]. These methods can be divided into two groups namely, the direct coupling of thiophene rings and the ring closure reactions of appropriate precursor compounds. Many different reaction conditions are used for the first approach of direct coupling including the Ullmann coupling of iodothiophenes with copper[2], the cross-coupling reaction of a dihalocompound with organometallics like magnesium, zinc or tin with a palladium or nickel catalyst[3], the copper(II)chloride oxidation of lithium derivatives[4] and the iodine oxidation of di-(2-thienyl) boranes[5]. In the second approach thiophenes have been synthesized by the ring closure reaction of diacetylenes with hydrogen sulfide[6] and diketosulfides with Lawesson's reagent[7], in which case small amounts of the β-isomer are obtained as



scheme 3.1 Thiophene synthesis by the ring-closure reaction of 1,4-diketones

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1 For a review see: Nakayama, J.; Konishi, T.; Hoshino, M. *Heterocycles* **1988**, *27*, 1731

2 a) Steinkopf, W.; v. Petersdorff, H.-J.; Gording, R. *Liebigs Ann. Chem.* **1937**, *527*, 272 b) Sease, J. W.; Zechmeister, L. *J. Am. Chem. Soc.* **1947**, *69*, 270

3 a) van Pham, C.; Burkhardt, A.; Shabana, R.; Cunningham, D. D.; Mark jr., H. B.; Zimmer, H. *Phosphorus, Sulfur, and Silicon* **1989**, *46*, 153 b) Tour, J. M.; Wu, R. *Macromolecules* **1992**, *25*, 1901 c) Bäuerle, P.; Pfau, F.; Schlupp, H.; Würtner, F.; Gaudl, K.-U.; Balparda Caro, M.; Fischer, P. *J. Chem. Soc., Perkin Trans. 2* **1993**, 489 d) Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Chem. Mater.* **1993**, *5*, 430

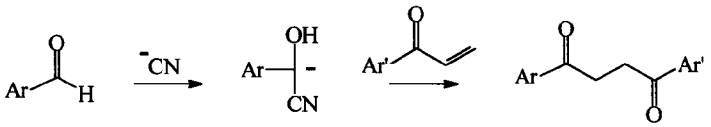
4 a) Kagan, J.; Arora, S. K.; *Heterocycles* **1983**, *20*, 1937 b) Yasser, A.; Delabouglise, D.; Hmyene, M.; Nessak, B.; Horowitz, G.; Garnier, F. *Adv. Mater.* **1992**, *4*, 490 c) Faïd, K.; Leclerc, M. *J. Chem. Soc., Chem. Commun.* **1993**, 962

5 Kagan, J.; Arora, S. K. *Tetrahedron Lett.* **1983**, *24*, 4043

6 Schulte, K. E.; Reisch, J.; Hörner, L. *Chem. Ber.* **1962**, *95*, 1943

7 Nakayama, I.; Nakamura, Y.; Murabayashi, S.; Hoshino, M. *Heterocycles* **1987**, *26*, 939

well. Furthermore, thiophenes have been synthesized by the cyclization reaction of 1,4-diketones with hydrogen sulfide[8], P_2S_5[9,10] or Lawesson's reagent[11,12]. The 1,4-diketones in turn have been prepared by the Friedel-Crafts reaction of thiophene with succinoyl chloride[13], oxidative dimerization of acetyl aryl compounds either as the lithium anions with copper(II) chloride[14] or as the silyl-enol ethers with silver oxide[15] and through the Michael addition of cyanohydrin anions to unsaturated carbonyl compounds. The latter approach is known as the Stetter reaction[16] (scheme 3.2). The Stetter reaction was actually observed by Smith as early as 1890[9].

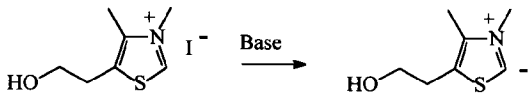


scheme 3.2 The Stetter reaction

The successful synthesis in our laboratories of α-terthienyl[12] and, more recently, of substituted oligomers of thiophene[17], prompted us to investigate in detail the scope and limitations of the procedure, in which the Stetter reaction is used in combination with the subsequent ring closure reactions of the 1,4-diketones with Lawesson's reagent.

3.1.1 The mechanism of the Stetter reaction

The Stetter reaction is based on the Michael addition of a cyanohydrin to an α,ß-unsaturated carbonyl compound, to give a 1,4-diketone (scheme 3.2). The catalyst is either a cyanide ion or an ylide. The latter is made in situ by the deprotonation of a thiazolium salt, which shows catalytic features similar to the cyanide ion (figure 3.1). The mechanism of the Stetter reaction is outlined in scheme 3.3. Addition of the catalyst to the aldehyde yields the cyanohydrin anion (the donor, **3.2**),



3.1

figure 3.1

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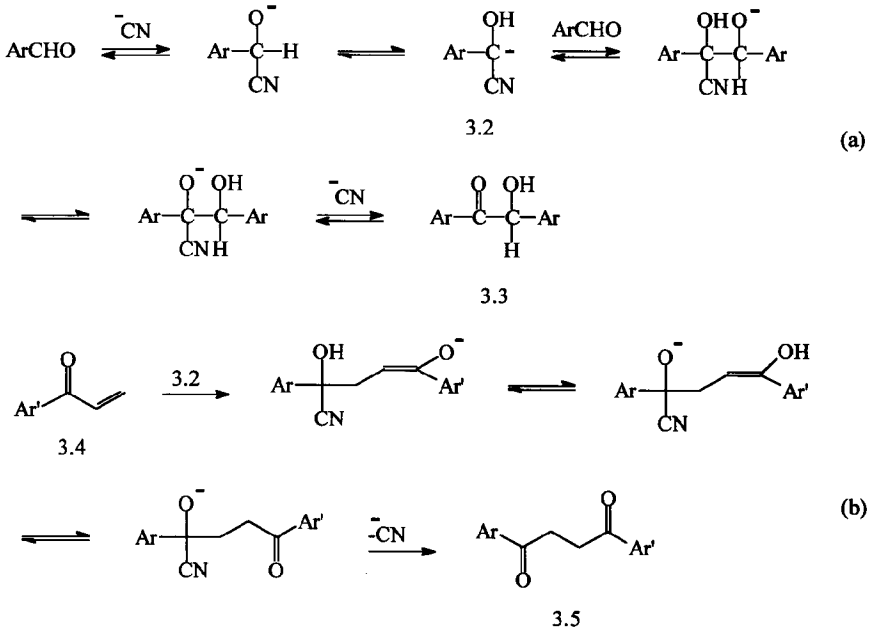
8 Wynberg, H.; Wiersum, U. *J. Org. Chem.* **1965**, *30*, 1058
9 Smith, A. *J. Chem. Soc.* **1890**, *57*, 643
10 Scheeren, J. W.; Oomes, P. H. J.; Nivard, R. J. F. *Synthesis* **1973**, 149
11 Shridhar, D. R.; Jogibhukta, M.; Rao, P. S.; Handa, V. K. *Synthesis* **1982**, 1061
12 Wynberg, H.; Metselaar, J. *Synth. Commun.* **1984**, *14*, 1
13 Merz, A.; Ellinger, F. *Synthesis* **1991**, 462
14 Ito, Y.; Konoike, T.; Harada, T.; Saegusa, T. *J. Am. Chem. Soc.* **1977**, *99*, 1487
15 Ito, Y.; Konoike, T.; Saegusa, T. *J. Am. Chem. Soc* **1975**, *97*, 649
16 a) Stetter, H. *Angew. Chem.* **1976**, *88*, 695 b) Stetter, H.; Kuhlmann, H. *Org. React.* **1991**, *40*, 407
17 ten Hoeve, W.; Wynberg, H.; Havinga, E. E.; Meijer, E. W. *J. Am. Chem. Soc.* **1991**, *113*, 5887

which in turn can add to the α,ß-unsaturated carbonyl moiety (the acceptor, **3.4**), affording the 1,4-diketone **3.5** (eq. b). However, the donor can also add to a second aldehyde molecule to form the α-hydroxy ketone **3.3** (benzoin), in what is known as the benzoin condensation (eq. a). Since the benzoin condensation is reversible and the Michael addition of the cyanohydrin to the α,ß-unsaturated carbonyl moiety is irreversible under the reaction conditions employed, the reaction is driven to completion via the 1,4-addition path (eq b)



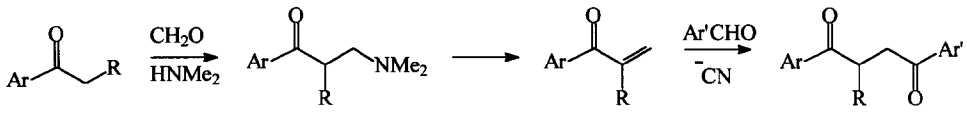
scheme 3.3 The mechanism of the Stetter reaction

The reaction is fairly general, but some limitations have been established with respect to the substitution pattern of the different aromatic rings when NaCN is employed as the catalyst[18]. Aryl aldehydes may bear neutral or electron withdrawing groups, but electron donating substituents hamper the Stetter reaction. The reactivity of the Michael acceptor seems not to be influenced by the nature of the substituents. Substituents that may be employed as solubilizing side-chains in the target oligomers, therefore, can be introduced in the aromatic moiety of the donor, unless the side-chain is electron donating, or at the aromatic moiety of the acceptor. Alternatively, solubilizing functionalities can be attached to the aliphatic moiety of the acceptor. In this case the side-chain has an influence on the reactivity of the acceptor. The α,β-unsaturated ketones used in the Stetter reaction

18 Phillips, R. B.; Herbert, S. A.; Robichaud, A. J. *Synth. Commun.* **1986**, *16*, 411

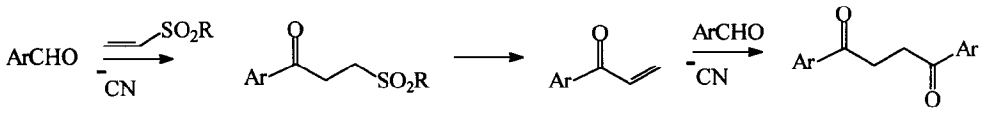
can be prepared independently or in-situ during the reaction. A variety of precursors and modified α,β-unsaturated ketones have been used[16]. The different types of Michael acceptors and their syntheses are outlined in schemes 3.4 to 3.8 below.

-The Mannich base is readily synthesized from the aryl methyl ketones (R=H) by reaction with formaldehyde and an amine, usually dimethylamine. Conversion into the diketone proceeds via the elimination of the amine and subsequent addition of the cyanohydrin to the generated α-β-unsaturated ketone (scheme 3.4). When propionyl aryl compounds are used, substituted diketones are obtained (R= CH_3).



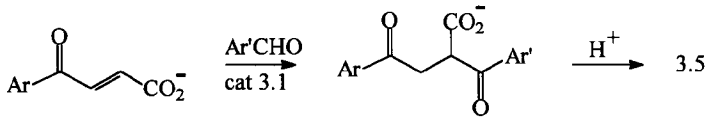
scheme 3.4

-Ethenylsulfonyl compounds are commercially available. Diketones are obtained in a three-step addition-elimination mechanism (scheme 3.5). An advantage of this approach is the availability of the Michael acceptor. The applicability, however, is limited due to the fact that only symmetrical diketones can be prepared and that the synthesis is accompanied by the production of the corresponding disulfone.



scheme 3.5

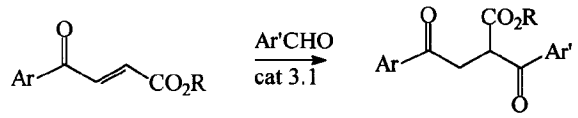
-Unsaturated acids, synthesized by the Friedel-Crafts acylation of aromatic compound with maleic anhydride, are employed as their sodium salts and afford diketones after spontaneous decarboxylation, during acidic workup (scheme 3.6). When unsaturated acids are used, the choice of catalyst is limited to the thiazolium salts, due to the possible 1,4-addition of the cyanide ion. Alternatively, β-bromo keto acids can be used as precursor compounds for the Michael acceptor that can be converted to the unsaturated acids upon base induced elimination of hydrogen bromide.



scheme 3.6

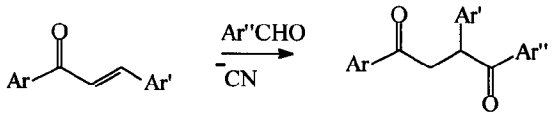
-Unsaturated esters can be prepared by the esterification of the corresponding acids. Since these compounds contain two electron withdrawing groups there are, theoreti-

cally, two different 1,4-additions possible, but the aromatic ketone moiety is the more activating one, and consequently only 1,4-addition relative to the ketone occurs. This affords the carboxylate ester substituted diketones (scheme 3.7). α,β-Unsaturated esters are very reactive and this may cause problems with respect to storage and side reactions. These difficulties can be circumvented by the use of β-bromo esters as precursor compounds.



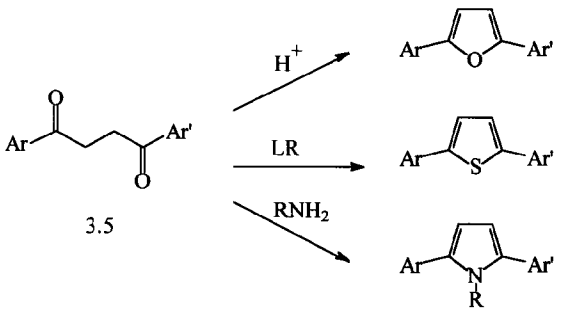
scheme 3.7

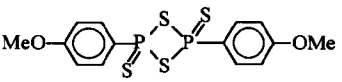
-Chalcones are readily synthesized by the condensation of aryl methyl ketones with aryl aldehydes. Chalcones are activated enones and give the aryl substituted diketones in good yields (scheme 3.8). Substituents can be introduced on the aryl groups.



scheme 3.8

Cyclization of 1,4-diketones affords furans, pyrroles and thiophenes. Furans are made by the acid catalyzed ring closure[9], and thiophenes are obtained upon ring closure with P_2S_5[9] or Lawesson's reagent[12]. Unsubstituted as well as N-substituted pyrroles are





Lawesson's reagent (LR)

scheme 3.9

formed upon the reaction of a 1,4-diketone with ammonia[9], ammonium carbonate[19], or ammonium acetate[12] and primary amines[20], respectively (scheme 3.9).

In this chapter we will describe the use of the Stetter reaction in the synthesis of a number of well-defined oligomers containing different aromatic rings. The scope and limitations for the synthesis of polymers using the Stetter reaction are discussed.

3.2 Oligomers

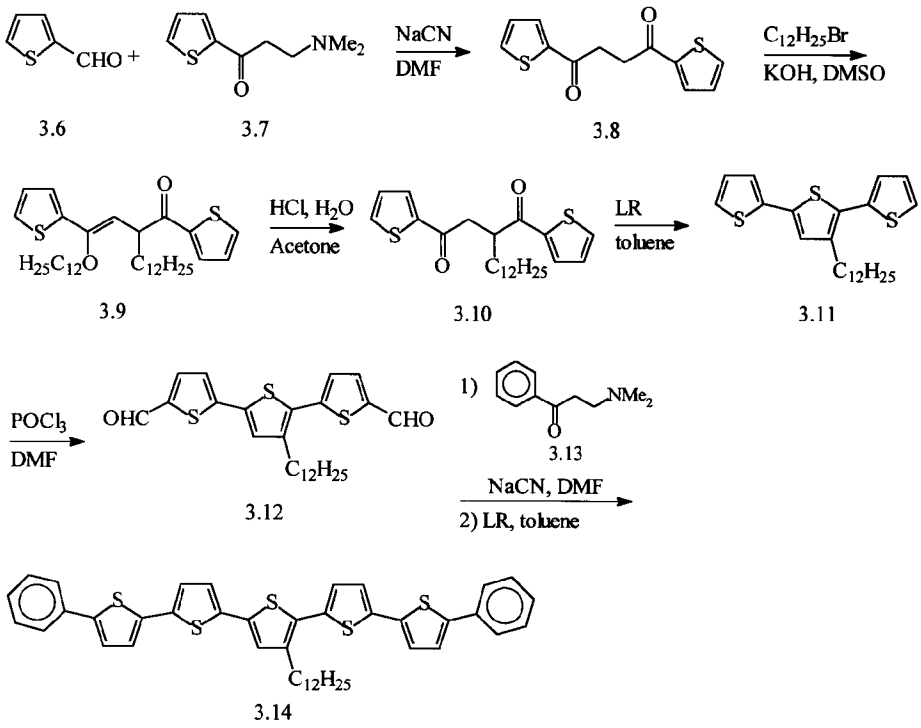
The Stetter reaction is a powerful method for the synthesis of a large variety of 1,4-diketones, both substituted and unsubstituted. Ring closure of the 1,4-diketones affords, for example, thiophenes. The combination of these two methods provides an attractive method for the synthesis of a diversity of well-defined aromatic oligomers. This approach allows the selective introduction of different kinds of substituents and a large variety of aromatic rings. In this section we will give examples of the synthesis of well-defined oligomers, containing different substituents and aromatic rings and we will determine the scope and limitations of the various Michael acceptors and donors. Solubilizing side chains are introduced either in the aldehyde functionality or in the double bond moiety of the Michael acceptor, or its precursor.

3.2.1 Synthesis

A first example of a well-defined oligomer synthesis is outlined in scheme 3.10. The synthesis of 3''-dodecyl-5,5''''-diphenyl-[2,2';5',2'';5'',2''';5''',2'''']quinquethiophene (**3.14**) is based on a combination of the Stetter reaction and subsequent cyclization with Lawesson's reagent (LR) to afford the thiophene ring. Introduction of the dodecyl side chain was accomplished by alkylation of the diketone **3.8**, which after ring closure with Lawesson's reagent afforded the dodecyl substituted terthienyl **3.11**. The introduction of the side chain via the alkylation is effective when applied to symmetrical diketones but is not very feasible when tetraketones are used since the alkylation does not discriminate between the two methylene groups of the 1,4-diketone moiety. Alkylation of tetraketones, therefore, will afford a mixture of regioisomers. Consequently, the synthesis of tetraketones requires substituents attached to the dialdehyde. Thus, 1,4-di-thiophen-2-yl-butane-1,4-dione (**3.8**) was synthesized in 77% yield by the reaction of thiophene-2-carbaldehyde (**3.6**) and 3-dimethylamino-1-thiophen-2-yl-propan-1-one (**3.7**)[12] with

19 Young, D. M.; Allen, C. F. H. *Org. Synth. Coll. Vol.* **II**, 25
20 Stetter, H.; Schreckenberg, M. *Chem. Ber.* **1974**, *107*, 2453

NaCN as catalyst at room temperature[12]. Alkylation with n-dodecylbromide, subsequent hydrolysis of enol ether **3.9** and ring closure of diketone **3.10** with Lawesson's reagent (L.R.) afforded 3'-dodecyl-[2,2';5',2'']-terthienyl (**3.11**) in 20% overall yield[17]. Formylation of **3.11** under Vilsmeier-Haack conditions afforded dialdehyde **3.12** in 51% yield[21]. 3'-Dodecyl-[2,2';5',2'']-terthienyl-5,5''-dicarbaldehyde (**3.12**) was allowed to react with 3-dimethylamino-1-phenyl-propan-1-one (**3.13**)[22] and NaCN as catalyst (10 mol %) and the resulting tetraketone was ring closed with Lawesson's reagent (LR). This afforded 3''-dodecyl-5,5''''-diphenyl-[2,2';5',2'';5'',2''';5''',2'''']-quinquethiophene (**3.14**) as a soluble (>80 mg/ml in $CHCl_3$) red solid in 51% yield. The absorption maximum, recorded in $CHCl_3$, was found at 429 nm.



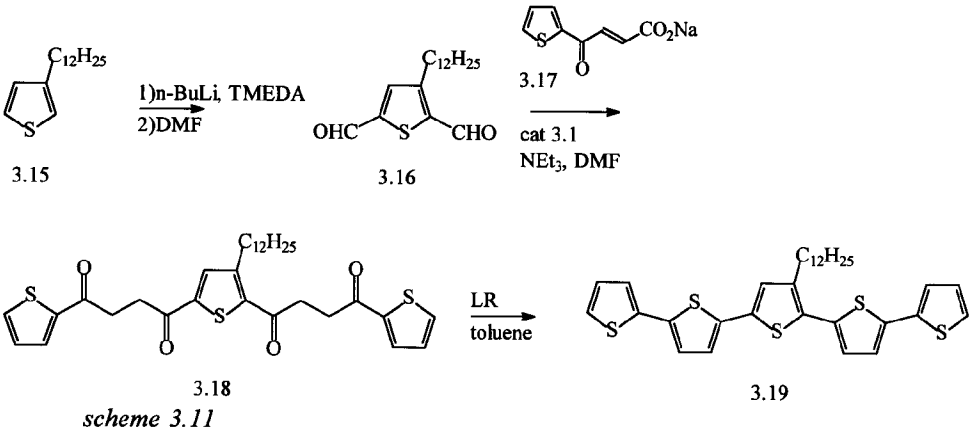
scheme 3.10

Clearly, the Stetter reaction has proceeded well, using Mannich bases **3.7** and **3.13** as precursors for the Michael acceptors. Dialdehyde **3.12**, however, has not provided much

21 ten Hoeve, W.; Wynberg, H. to be published

22 Vogel, A. I. *Textbook of practical organic chemistry* 5th Ed., Longman Inc. New York **1989** p 1053

information about the influence of substituents on the reactivity of aldehydes in the Stetter reaction, because the three substituents (two formyl groups and a n-dodecyl group) are located on different rings. To get a better insight in the influence of the substituents both the side chain and the aldehyde functionalities must be connected to the same ring. A dialdehyde of this type (**3.16**) has been used for the synthesis of 3''-dodecyl-[2,2';5',2'';5'',2''';5''',2'''']-quinquethienyl (**3.19**). The complete reaction sequence is outlined in scheme 3.11. 3-Dodecylthiophene (**3.15**) was transformed to the 2,5-dialdehyde **3.16** in 86% yield by quenching the bis-anion with DMF in analogy to the literature procedure for the unsubstituted thiophene[23]. Reaction with 4-oxo-4-thiophen-2-yl-but-2-enoic acid (**3.17**)[24] and catalyst **3.1** afforded tetraketone **3.18** in 44% yield. 5-(2-Hydroxyethyl)-3,4-dimethyl-1,3-thiazoliumiodide (**3.1**) was used as catalyst since cyanide ions cannot be used when unsaturated acids are employed as Michael acceptor. Ring-closure of the tetraketone with Lawesson's reagent afforded 3''-dodecyl-[2,2';5',2'';5'',2''';5''',2'''']-quinquethienyl (**3.19**) as an orange solid with a λ_{max} of 407.5 nm, recorded in $CHCl_3$, in a yield of 62%. Although the dodecyl functionality is slightly electron donating, the reactivi-



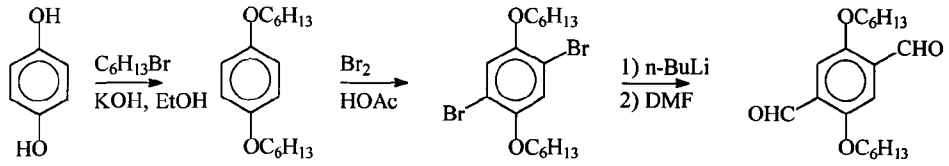
3.15 3.16 3.18 3.19

scheme 3.11

ty of dialdehyde **3.16** is not much lower than that of dialdehyde **3.12**. The lower overall yield of **3.19** compared to that of **3.14** (51% and 27% respectively) is mainly due to isolation and purification of tetraketone **3.18**. To investigate the influence of strongly electron donating substituents, 2,5-bis-hexyloxy-terephthaldehyde (**3.23**) was synthesized and subjected to the Stetter reaction. Since the Stetter reaction of aldehydes with electron donating substituents fails when cyanide ions are used[18], thiazolium salt **3.1** is the obvious choice of catalyst. Thus, 1,4-bis-hexyloxy-benzene (**3.21**)[25] was synthesized by alkylating

23 Feringa, B.; Hulst, R.; Rikers, R.; Brandsma, L. *Synthesis* **1988**, 316
24 Papa, D.; Schwenk, E.; Villani, F.; Klinsberg, E. *J. Am. Chem. Soc.* **1948**, *70*, 3356
25 Askari, S. H.; Rughooputh, S. D.; Wudl, F. *Synth. Met.* **1989**, *29*, E129

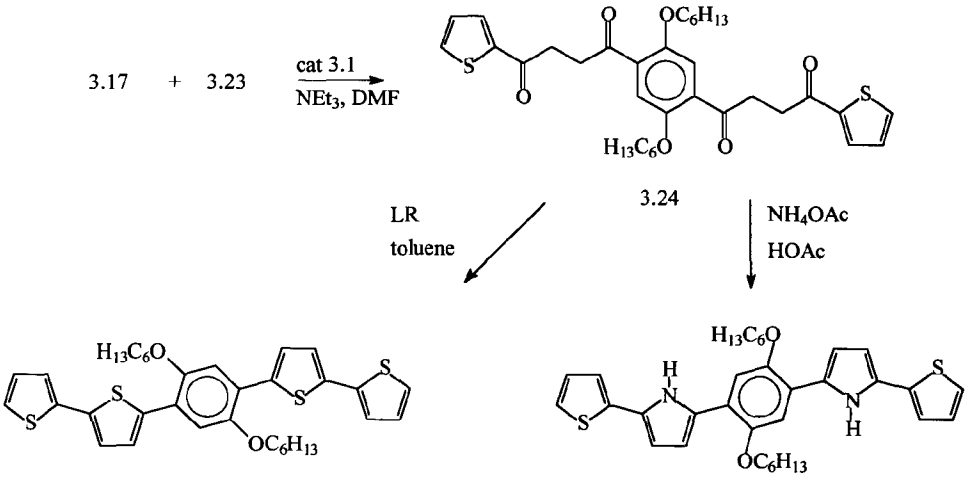
hydroquinone (**3.20**) with hexyl bromide and the dibromide **3.22** was obtained in 76% yield by the action of bromine in acetic acid[26]. Lithiation by bromine-lithium exchange with n-butyl lithium and quenching of the anion with DMF gave 2,5-bis-hexyloxy-terephthaldehyde (**3.23**) in 63% yield (scheme 3.12). Dialdehyde **3.23** was subjected to the



3.20 3.21 3.22 3.23

scheme 3.12

Stetter reaction with α,ß-unsaturated acid **3.17** and catalyst **3.1** and afforded 1,4-bis-(4-oxo-4-thiophen-2-yl-butyryl)-2,5-bis-hexyloxy-benzene (**3.24**) in a yield of 61%. Apparently, electron donating substituents do not hamper the Stetter reaction when catalyst **3.1** is used. Tetraketone **3.24** was converted to 1,4-bis-(5-(2,2'-bithiophen-5-yl)-2,5-bis-hexyloxy-benzene (**3.25**) in 86% yield by ring closure with Lawesson's reagent (scheme 3.13). Ring-closure with ammonium acetate afforded 1,4-bis-(5-thiophen-2-yl-[1H]-pyrrol-2-yl)-2,5-bis-hexyloxy-benzene (**3.26**) in a yield of 75% (scheme 3.13). Both



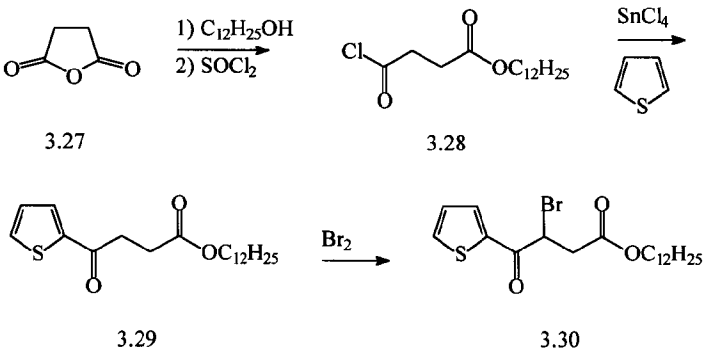
3.25 3.26

scheme 3.13

26 Underwood, H. W.; Baril, O. L.; Toone, G. C. *J. Am. Chem. Soc.* **1930**, *52*, 4087

compounds had an orange color with absorption maxima (recorded in $CHCl_3$) at 404.4 and 405.1 nm, respectively. The introduction of the pyrrole moiety increases the sensitivity of the compound toward oxidation as seen by the appearance of a second absorption signal in the UV spectrum at 550 nm upon exposure to air.

A variety of substituted aldehydes have been used in the Stetter reaction, resulting in soluble oligomers, after cyclization of the resulting diketones. A different approach to obtain soluble oligomers is the use of substituted Michael acceptors in the Stetter reaction. Substituents can be attached either to the aromatic ring or to the double bond, or its precursor, of the Michael acceptor. We will describe the use of the latter option. For this approach, it is not possible to use all Michael acceptors described in schemes 3.4 to 3.8, since the selective introduction of a substituent in the unsaturated acid moiety is far from trivial. Unsaturated keto-esters (see scheme 3.7) affords oligomers with the ester group as solubilizing functionality. To overcome problems with respect to storage of the unsaturated keto-esters, we used ß-bromo esters as precursor compounds. These are easily converted to the unsaturated esters by the elimination of hydrogen bromide under the basic reaction conditions employed in the Stetter reaction with the thiazolium salt **3.1** as catalyst. Thiophene was acylated with 3-chlorocarbonyl-propionic acid dodecyl ester (**3.28**), synthesized in two steps from succinic anhydride (**3.27**)[27] in 74% yield and the resulting keto ester **3.29** was treated with bromine[28] to give 3-Bromo-4-oxo-4-thiophen-2-yl-butyric acid dodecyl ester (**3.30**) in 83% yield (scheme 3.14). Bromide **3.30** was brought into reaction

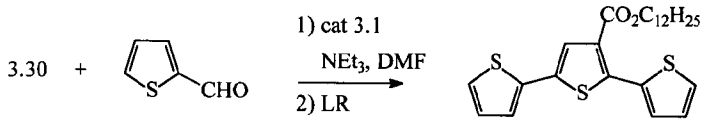


3.27 3.28 3.29 3.30

scheme 3.14

with 2-thiophene aldehyde (**3.6**), catalyst **3.1** (10 mol %) and triethylamine (3 equivalents). The resulting diketone was ring-closed with Lawesson's reagent affording [2,2';5',2'']-terthiophene-4'-carboxylic acid dodecyl ester (**3.31**) in 43% yield (based on **3.30**) as an oil that rapidly became colored (scheme 3.15). The reaction of [2,2']-bithienyl-5,5'-

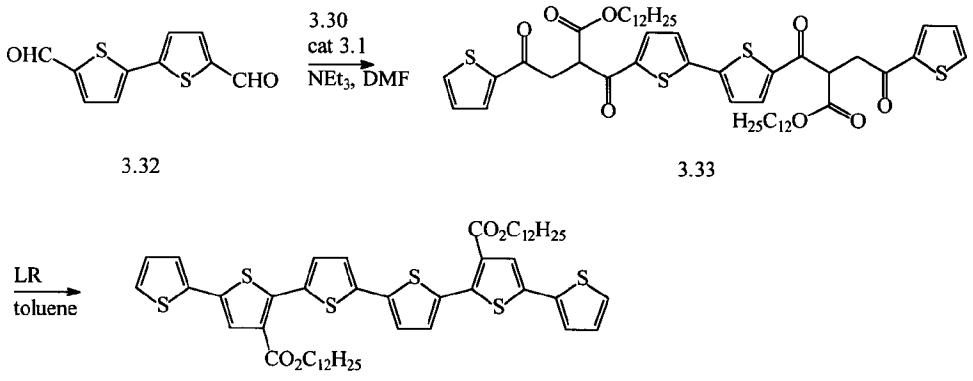
27 Cason, J. *Org. Synth. Coll. Vol.* **III**, 169
28 Knott, E. B. *J. Chem. Soc.* **1945**, 455



3.6 3.31

scheme 3.15

dicarbaldehyde (**3.32**, synthesized according to a literature procedure[29]) with ester **3.30** under the same reaction conditions as described in scheme 3.15 afforded tetraketone **3.33** in 88%. ^{1}H-NMR revealed that the all-keto isomer **3.33** was the only isomer present. Upon ring closure with Lawesson's reagent, [2,2';5',2'';5'',2''';5''',2'''';5'''',2''''']-sexithiophene-4',3''''-dicarboxylic acid didodecyl ester (**3.34**) was obtained in an isolated yield of 34% (scheme 3.16). ^{1}H-NMR of the crude reaction mixture showed the presence of an



3.32 3.33

3.34

scheme 3.16

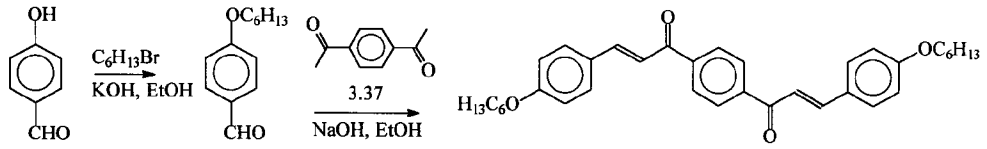
unsaturated keto ester arising from the retro-Michael reaction[30]. Compound **3.34** showed an increase in solubility relative to unsubstituted thiophene oligomers in common organic solvents (for a comparision; α-sexithienyl is insoluble in ether[4a], while α-quinquethienyl is insoluble in hexane[2b]. Compound **3.34** on the other hand is soluble in ether and can be recrystalized form hexane) In $CHCl_3$, the red microcrystalline compound **3.34** had an absorption maximum of 434.4 nm.

Since the ester substituent attached to the double bond of the Michael acceptor has proven to be very effective for the Stetter reaction, other Michael acceptors with

29 Curtis, R. F.; Phillips, G. T. *Tetrahedron* **1967**, *23*, 4419

30 March, J. *"Advanced Organic Chemistry"*, 3rd ed., John Wiley and Sons, Inc., **1985**, p 918

substituents attached to the double bond, or its precursor, were examined as well. Chalcones have frequently been used in the Stetter reaction[31]. However, when unsubstituted chalcones are used (see scheme 3.8, Ar'= phenyl), the only side group incorporated in the resulting oligomer, after cyclization of the diketone, is the phenyl ring, and the solubilizing effect of the phenyl ring is limited. Therefore, we have introduced an alkoxy functionality in the chalcone. The synthesis of the substituted chalcone **3.38** is outlined in scheme 3.17. p-Hydroxybenzaldehyde (**3.35**) was alkylated with n-hexyl bromide to give **3.36** in 72 % yield. Condensation of **3.36** with 1,4-diacetylbenzene (**3.37**) afforded chalcone **3.38** in 45% yield. Notwithstanding the presence of the substituents the solubility



3.35 3.36 3.38

scheme 3.17

of 1,4-bis-[3-(4-hexyloxy-phenyl)-acryloyl]-benzene (**3.38**) was limited (<10 mg/ml in DMF at 25°C). This low solubility probably arises from the fact that the alkoxy functionalities are end groups of the π-system and not side chains. It is known[32] for oligothiophenes that end groups are almost ineffective as solubilizing functionalities. Due to this limited solubility it was not possible to add a solution of the chalcone to a mixture of an aldehyde and NaCN. Slow addition was anticipated to prevent the addition of the cyanide ion to the chalcone[33]. We employed catalyst **3.1**. Thus, benzaldehyde (**3.39**) and chalcone **3.38** were allowed to react at 80°C for four days affording tetraketone **3.40** in 8%. Ring-closure with ammonium acetate afforded 2,5-Bis-[4-(4-hexyloxy-phenyl)-5-phenyl-1H-pyrrol-2-yl]-benzene (**3.41**) in 50% (scheme 3.18). Although oligomer **3.41** is far more soluble (>50 mg/ml in $CHCl_3$ at 25°C) than compound **3.38**, the low yield of tetraketone **3.40** strongly limits the applicability of chalcon **3.38** in the Stetter reaction. For the introduction of a methyl substituent in the Michael acceptor, the substituted Mannich base was used, synthesized as depicted in scheme 3.19. 1,4-Bis-propionyl benzene (**3.43**) was synthesized by the reaction of terephthaldehyde (**3.42**) with ethyl magnesiumiodide and subsequent oxidation of the alcohol in 38% yield. Condensation with

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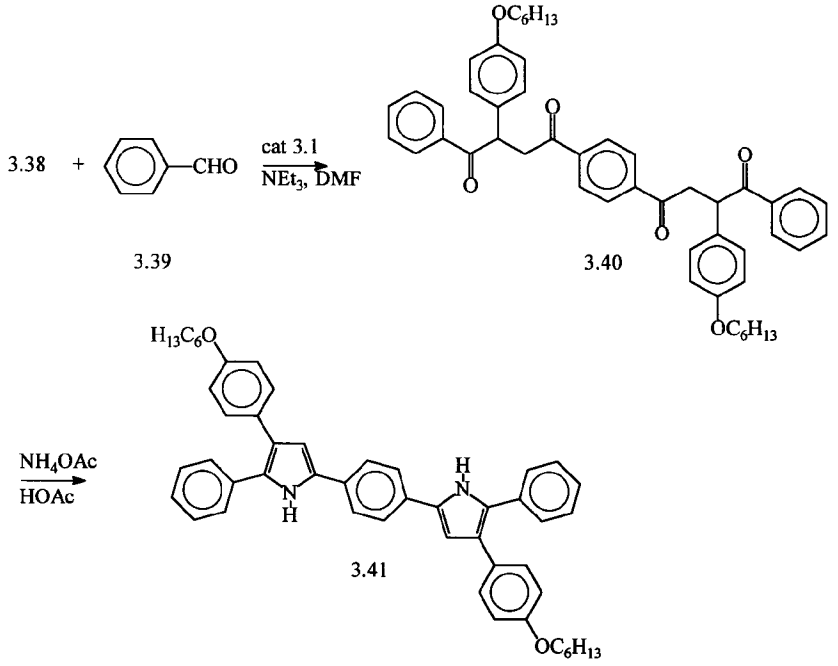
31 a) Maud, J. M.; Haudry, P.; Llewellyn, G.; Vlahov, A.; Hepburn, A. R.; Marshall, J. M.; Goldie, D. M. *Synth. Met.* **1993**, *55-57*, 851. b) Kankare, J.; Lukkari, J.; Pasanen, P.; Sillanpää, R.; Laine, H.; Harmaa, K.; Visy, C. *Macromolecules* **1994**, *27*, 4327.

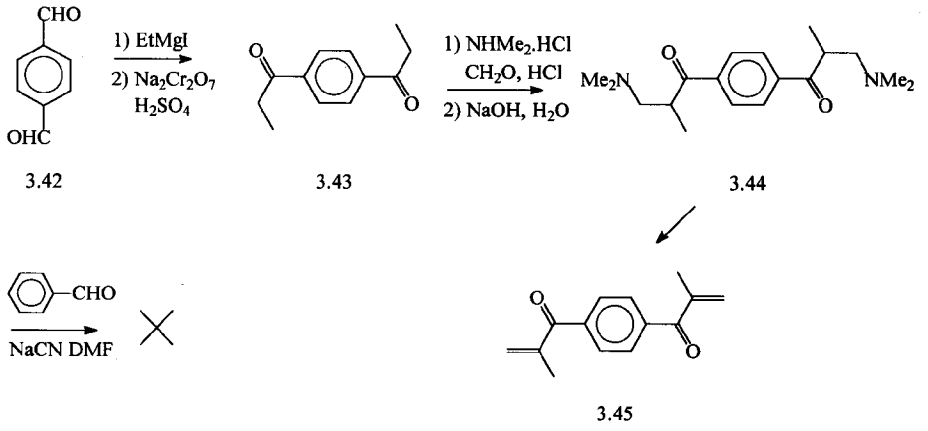
32 Garnier, F.; Yasser, A.; Hajlaoui, R.; Horowitz, G.; Deloffre, F.; Servet, B.; Ries, S.; Alnot, P. *J. Am. Chem. Soc.* **1993**, *115*, 8716

33 Ciller, J.A.; Seoane, C.; Soto, J. L. *Liebigs Ann. Chem.* **1985**, 51



scheme 3.18

dimethylamine and formaldehyde afforded the bis-Mannich base **3.44** in 28% yield. However, the corresponding tetraketone could not be isolated from the reaction of **3.44** with benzaldehyde, the only isolated compound was the elimination product **3.45**. The electron donating methyl group reduces the reactivity of the Michael acceptor considerably.



scheme 3.19

3.2.2 Absorption spectroscopy

To obtain information about the influence of the substituents on the effective conjugation length of the oligomers, we have determined the λ_{max} values and compared these data to the λ_{max} of unsubstituted oligothiophenes consisting of an equal number of rings. The data are summarized in table 3.1 Oligomer **3.14**, consisting of five thiophene rings and two phenyl end-groups displays a λ_{max} of 429 nm, whereas for unsubstituted septithienyl the λ_{max} is found at 440 nm. The oligomers with five rings; **3.19**, **3.25** and **3.26** have λ_{max} of 407.5 nm, 404.4 nm and 405.1 nm, respectively. Unsubstituted quinquethienyl has a λ_{max} of 416 nm. Alkyl substituents have a considerable influence, although there is only one substituent present in oligomer **3.14** and **3.25**, the hypsochromic shift is 11 and 8.5 nm, respectively. The positioning of the alkyl group, dividing the compounds into two parts probably accounts for the significant decrease. Oligomer **3.14** displays an extra blue shift as a result of the phenyl groups. Electron donating substituents cause a red shift[34], and the hexyloxy-substituted benzene ring in compound **3.25** has an influence similar to that of a thiophene ring; the λ_{max} of the five-ring oligomers are almost the same. However, the ester substituents in oligomer **3.34** have no negative influence on the conjugation length. A comparison with the unsubstituted and the didodecyl substituted sexithienyl derivatives shows this clearly. Oligomer **3.34** has a λ_{max} of 434.4 nm, whereas

table 3.1 UV absorption maxima of selected oligomers

compound	number of rings (n)	λ_{max} ($CHCl_3$) (nm)	unsubstituted thiophenes n	unsubstituted thiophenes λ_{max} ($CHCl_3$) (nm)
3.14	7	429	7	440[a] (in benzene)
3.19	5	407.5	5	416[a]
3.25	5	404.4		
3.26	5	405.1		
3.34	6	434.4	6	432[b] 416[b,c]

a) see ref 1. b) Bäuerle, P.; Segelbacher, U.; Gaudl, K.-U.; Huttenlocher, D.; Mehring, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 76. c) λ_{max} of 3'''',4'-didodecyl-α-sexithienyl.

α-sexithienyl has a λ_{max} of 432 nm. Didodecyl-α-sexithienyl on the other hand displays a

34 Ruiz, J. P.; Dharia, J. R.; Reynolds, J. R.; Buckley, L. J. *Macromolecules* **1992**, *25*, 849

maximum absorption value of 416 nm.

3.2.3 Discussion

Ester groups form a new class of solubilizing moieties, when attached directly to the aromatic backbone of thiophene oligomers as in compound **3.34**, and can be readily introduced using unsaturated keto-ester precursor **3.30** in the Stetter reaction. High yields of ketone **3.33** are obtained, with complete regioregularity of the ester groups. Synthesis of the unsaturated keto-esters can be accomplished by the esterification of the acids, but the bromide precursor has a higher stability, and therefore is easier to handle and purify. Elimination of hydrogen bromide from bromide **3.30** is carried out in situ by triethylamine, already present in the reaction mixture for the generation of the catalyst from thiazolium salt **3.1**. Ring closure of tetraketone **3.33** with Lawesson's reagent affords thiophene oligomer **3.34**, but only in a yield of 34%. This moderate yield arises from the fact that probably due to the elevated temperature of the cyclization reaction, retro Michael reactions occur[30]. The ester functionality of **3.34** has an excellent solubilizing effect but does not reduce the conjugation length as is seen for the alkyl substituted thiophene oligomers. Two examples of substituted oligothiophenes with an λ_{max} surpassing that of the unsubstituted parent compounds have been described[32,35], but in these instances the alkyl substituents are attached at the α-positions of the exterior thiophene rings, therefore are end groups, and do not increase the solubility. For the surprisingly high λ_{max} of compound **3.34**, the explanation must be found in the geometry of the ester functionalities. The ester functionality is planar and therefore can have a perpendicular orientation with respect to the thiophene ring, with minimal interaction. Consequently, the thiophene rings in **3.34** can maintain a co-planar orientation with maximal conjugation. For an alkyl substituent in for example compound **3.19**, there remains considerable interaction between two protons and the thiophene rings in the perpendicular orientation, because of the sp^3-configuration of the methylene group, resulting in the observed decrease of the λ_{max} relative to the unsubstituted analog. Alternatively, the high λ_{max} of compound **3.34** can be explained in terms of an active interaction between the ester functionality and the thiophene ring, particularly between the lone-pairs of the carbonyl group and the empty d-orbitals of sulfur at the adjacent thiophene ring. This interaction, a kind of back-donation, forces the two adjacent thiophene rings into co-planarity. This geometry, however, the

35 Havinga, E. E.; Rotte, I.; Meijer, E. W.; ten Hoeve, W.; Wynberg, H. *Synth. Met.* **1991**, *41-43*, 473

ester group is in conjugation with the thiophene backbone. Since ester groups are electron withdrawing, this would result in a blue shift of the λ_{max} of compound **3.34**[36]. The observed λ_{max}, however, does not display a blue shift, and therefore the gain in conjugation by the forced coplanarity compensates for the blue shift induced by the electron withdrawing ability of the ester functionality. The first explanation, with the ester group perpendicular relative to the tiophene rings, the ester group is not in conjugation with the thiophene backbone, and the only effect is the gain in coplanarity of the thiophene rings, making this the most plausible explication for the high λ_{max} of compound **3.34**.

The introduction of substituents in chalcone **3.38** is accomplished using substituted benzaldehyde **3.36**. The solubility of **3.38**, however, is limited because the solubilizing functionalities are end groups. This low solubility prevents the use of NaCN as catalyst, since the cyanide can add 1,4 to chalcone **3.38**. The low yield of tetraketone **3.40** obtained by the thiazolium ylide catalyzed reaction of **3.38** with benzaldehyde arises from the fact that the thiazolium derived 'cyanohydrin' is less reactive than its cyanide counterpart. This difference in reactivity stems from the fact that the thiazolium derived 'cyanohydrins' are ylides and therefore are intramolecularly stabilized, whereas the cyanide cyanohydrin species are salts. Furthermore, chalcone **3.38** has an alkoxy substituent at the para position of the phenyl group. The alkoxy group is electron donating and therefore reduces the electron withdrawing ability of the phenyl group attached to the double bond. Consequently, **3.38** is less reactive in the Michael reaction. A similar decrease in reactivity is observed for substituted Mannich base **3.34** where the electron donating methyl group is attached adjacent to the amine functionality. However, in this instance the reduction of reactivity of **3.34** as Michael acceptor is so drastic that the cyanide catalyzed addition of benzaldehyde is not found at all.

For the synthesis of 1,4-diketones, using the Stetter reaction, both the unsubstituted Mannich bases **3.7** and **3.13** and unsaturated acid **3.17** have proven to be good Michael acceptors that afford the diketones in high yields. An advantage is the one step synthesis of acid **3.17** compared with the three steps required for the preparation of the free Mannich bases. A combination of two factors is responsible for the successful use of dialdehydes **3.16** and **3.23**, containing electron donating substitutents. The first reason is that the aldehydes contains two formyl groups, so the electron donating effect of the electron donating substituents is, at least partly, neutralized by the second aldehyde functionality. On the other hand, the cyanide catalyzed reaction of the hexyloxy substituted aldehyde **3.23** with Mannich base **3.13** fails, so this is not the only reason. Secondly, the unsaturated acid **3.17** is a better Michael acceptor than the Mannich bases **3.7** and **3.13**.

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36 Robitaille, L.; Leclerc, M. *Macromolecules* **1994**, *27*, 1847

Ring-closure with Lawesson's reagent gives high yields of the corresponding thiophenes, except for the ester substituted diketones. Pyrroles have been obtained in good yields upon ring closure with ammonium acetate. These compounds are, as could be expected, more sensitive toward oxidation than their thiophene counterparts. From UV analysis it is clear that alkyl substituents have a negative effect on the effective conjugation length. This blue shift arises from the steric hindrance between the substituent and the adjacent thiophene ring. With the introduction of phenyl rings, the λ_{max} is shifted further to the blue region, but alkoxy substituents compensate for this effect. This relative red shift arises from the electron donating capacity of the alkoxy groups, but also because alkoxygroups are sterically smaller compared to alkyl functionalities[37]. All these compounds on the other hand are far more soluble than their unsubstituted counterparts. These results show that substitution of aromatic compounds by alkyl groups is not favorable for the highest possible conjugation length, but the increase in solubility compensates for the decrease in conjugation.

3.3 Polymers

The combination of the Stetter reaction and subsequent cyclization of the 1,4-diketones as for example in scheme 3.11 has proven very effective for the synthesis of well-defined oligomers, containing a variety of substituents and aromatic rings. We therefore decided to investigate the use of this method for the preparation of π-conjugated polymers. For the synthesis of 1,4-diketone polymers, using the Stetter reaction, there are two different approaches. The first is the use of two monomers, one containing two donor moieties and the other two acceptor moieties; an AA-BB-polymerization. Secondly, monomers containing both an acceptor and a donor functionality, can be polymerized in an A-B-polymerization. Both approaches have been investigated and the results are given below.

3.3.1 AA-BB-Polymerization

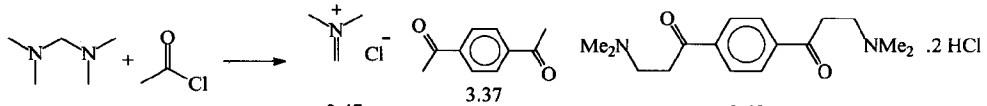
For the synthesis of poly-1,4-diketones using the Stetter reaction in an AA-BB-polymerization, both dialdehydes as well as bis-Michael acceptors are required. The synthesis of several dialdehydes has been described in the previous section. Thiophene-2,5-dicarbaldehyde (**3.46**) was synthesized in 71% yield according to a literature procedure[23] (scheme 3.20). Although several Michael acceptors have proven useful for the synthesis of

37 Faid, K.; Cloutier, R.; Leclerc, M. Synth. Met. **1993**, *55-57*, 1272

3.46

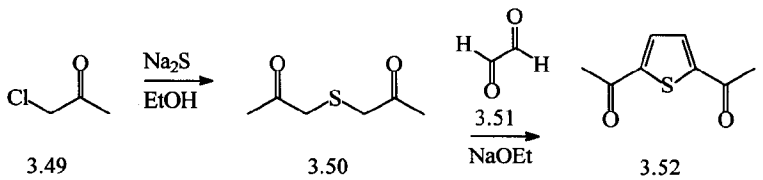
scheme 3.20

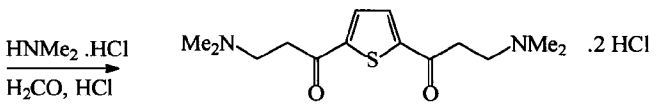
oligomers, not all of them are suitable as monomers since for synthesis of a polymer high conversions of the reactions are required. Obvious reasons are the low reactivity of chalcones and substituted Mannich bases, but also the expected insolubility of bis-unsaturated acids. Although the corresponding 1,4-diketones have been obtained in high yields, carboxylic esters are not suitable because in the cyclization reaction moderate yields have been obtained. Therefore, we have decided to use the Mannich base as precursor for the Michael acceptor. The synthesis of several bis-Mannich bases is outlined in schemes 3.21 to 3.23 below. The bis-Mannich base **3.48** of 1,4-diacetylbenzene (**3.37**) can be synthe-



scheme 3.21

sized using the standard method[38] with paraformaldehyde, dimethylamine hydrochloride and hydrochloric acid in ethanol. Higher yields, up to 84%, were obtained when dimethyl(methylene)ammonium chloride (**3.47**) was used[39] (scheme 3.21). Although 2,5-





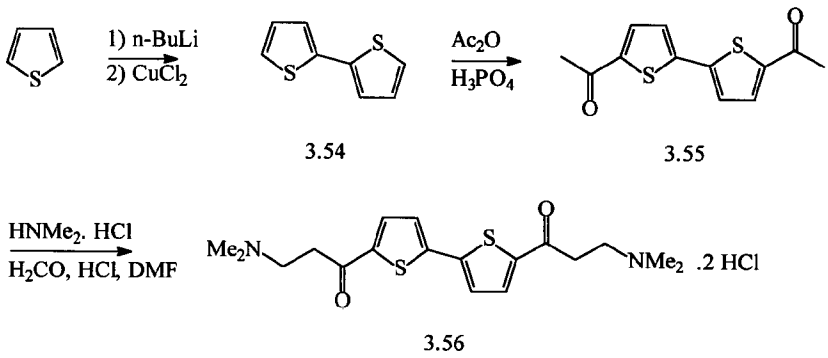
3.53

scheme 3.22

38 Tramontini, M. *Synthesis* **1973**, 703

39 Kinast, G.; Tietze, L.-F. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 239

diacetylthiophene (**3.52**) was readily synthesized in two steps from chloroacetone (**3.49**), sodium sulfide and glyoxal (**3.50**) in 20% overall yield as outlined in scheme 3.22[40], the synthesis of the bis-Mannich base **3.53** was troublesome. From the reaction with dimethylamine and formaldehyde or dimethyl(methylene)ammonium chloride the product was isolated with a purity of approximately 85 to 90%. We were not able to increase the purity by crystallization, due to the amorphous nature of **3.53**. Therefore, the bithienyl derivative was synthesized as depicted in scheme 3.23. [2,2']-Bithienyl (**3.54**) was synthesized by the $CuCl_2$ oxidation of the anion derived from thiophene and n-BuLi according to a modified literature procedure[4] and acylated in analogy with a literature procedure[41] with acetic anhydride and phosphoric acid affording 5,5'-diacetyl-[2,2']-bithienyl (**3.55**) in 28% yield. The bis-Mannich base **3.56** was obtained upon the acid catalyzed condensation of **3.55** with dimethylamine and para-formaldehyde in DMF as solvent. In this case the product could be isolated with high purity.

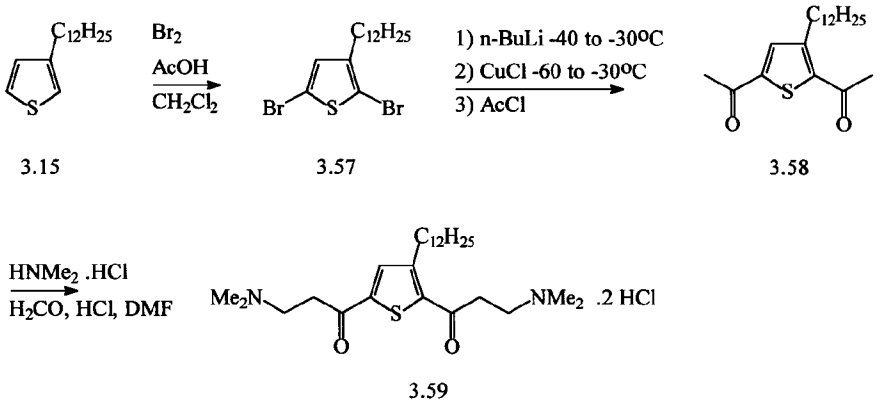


scheme 3.23

Since alkyl groups attached to the aliphatic moiety of the Mannich base, as in compound **3.44** drastically reduces the reactivity in the Stetter reaction, solubilizing side chains have to be attached to the aromatic rings. Synthesis of the dodecyl substituted thiophene bis-Mannich base is outlined in scheme 3.24. The diacetyl compound was synthesized by the acylation of the cuprate[42] since the introduction of two acyl groups via Friedel-Craft acylation is ineffective[43]. 3-Dodecylthiophene (**3.15**) was brominated afford-

40 Miyahara, Y. *J. Heterocycl. Chem.* **1979**, *16*, 1147
41 Wynberg, H.; Logothetis, A. *J. Am. Chem. Soc.* **1956**, *78*, 1958
42 Smith Jr., M. R.; Gilman, H. *J. Organomet. Chem.* **1972**, *42*, 1
43 Diacylation of thiophene has been reported, but only in a yield of six percent. see: Hartough, H. D.; Kosak, A. I. *J. Chem. Soc.* **1947**, *69*, 1012

ing the dibromide **3.57** in 91%. The dibromide **3.57** was converted to the cuprate and quenched with acetylchloride affording 2,5-diacetyl-3-dodecylthiophene (**3.58**) in 63% yield (scheme 3.24). Subsequent condensation with dimethylamine and paraformaldehyde

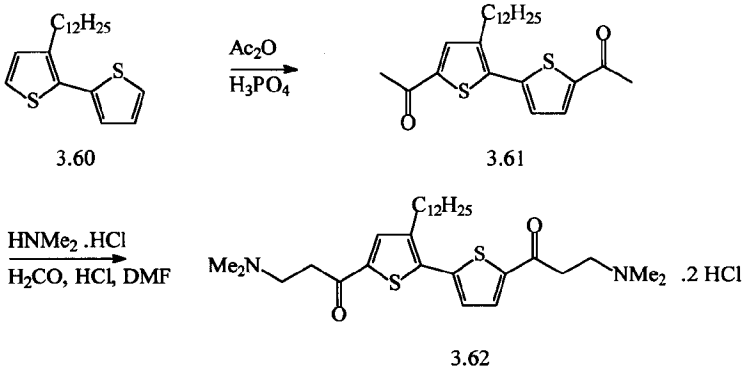


3.15 3.57 3.58

3.59

scheme 3.24

afforded the bis-Mannich base **3.59** as the hydrochloride salt. However, the stability of the product was very low; within a few hours, the yellow solid completely lost its initial solubility in water. Therefore, other substituted thiophene derivatives were used. The bis-Mannich bases of 3'-dodecyl-[2,2']-bithienyl (**3.60**) and 3''-dodecyl-[2,2';5',2'']-terthienyl (**3.11**) were synthesized as outlined in scheme 3.25 and 3.26, respectively. The diacetyl derivatives **3.61** and **3.63** were prepared by the acylation with acetic anhydride in 54% and 35% yield, respectively, and were transformed into the bis-Mannich bases **3.62** and **3.64**



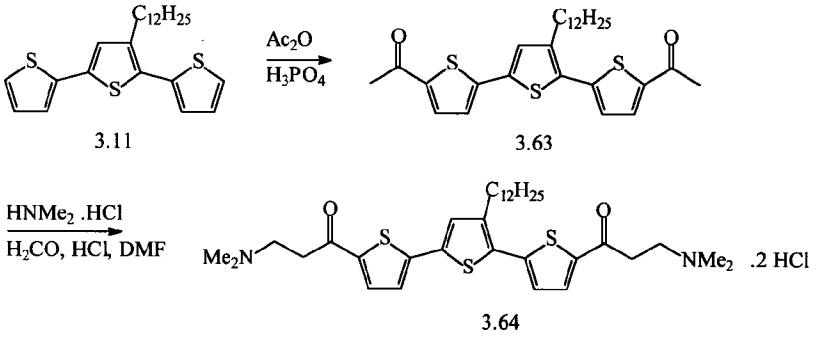
3.60 3.61

3.62

scheme 3.25

with dimethylamine and paraformaldehyde and were obtained as the hydrochloride salts in yields of 40% and 70%, respectively. Of the last two compounds, bithienyl derivative **3.62** suffered from identical problems as the thiophene analog, although the stability was

higher. Consequently, only the terthienyl derivative **3.64**, obtained in a yield of 70%, could be used in the polymerization reaction.

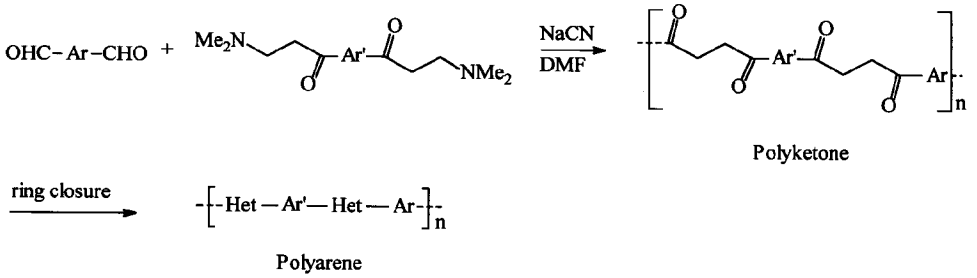


scheme 3.26

Polymerization (scheme 3.27 and table 3.2) was carried out by dissolving equimolar amounts of both a aldehyde (**3.42**, **3.46**, **3.12**, or **3.16**) and a free Mannich base (obtained from the hydrochloric acid salt (**3.48**, **3.56** or **3.64**) upon treatment with ammonia and extraction of the amine with CH_2Cl_2) in DMF in a nitrogen atmosphere. Upon addition of ten to twenty mol percent sodium cyanide, the solution turned dark as a result of cyanohydrin formation. The reaction mixture was stirred at room temperature for a few days. During the reaction, the mixtures became viscous and all the products of table 3.2, except poly-1,4-diketone **3.75**, precipitated. The reaction was terminated by pouring the mixture into water and the resulting solid was collected, washed with water, ethanol and dried. All compounds were insoluble in organic solvents except the last entry; poly-1,4-diketone **3.75** prepared from 3-dodecylthiophene-2,5-dicarbaldehyde (**3.16**). The insolubility of poly-1,4-diketone **3.72** can be explained in terms of the ratio alkyl side chain versus aromatic rings. With respect to solubility, the 1,4-diketone moiety is comparable with the thiophene ring, and polyketone **3.72** can be regarded as having one alkyl substituent on every four units. Polythiophene derivatives with one alkyl substituent on every three thiophene rings already display a diminished solubility[44]. Therefore, it is not surprising that a decrease in side chain content is accompanied with a further decrease in solubility. Poly-1,4-diketones were transformed to the thiophenes by ring-closure with Lawesson's reagent. Due to the insolubility of the polymers, the solvent greatly affected the degree of conversion of the diketone. Going from benzene via toluene, xylene, chlorobenzene to dichlorobenzene, the IR spectra of the product displayed a significant decrease in carbonyl

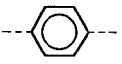
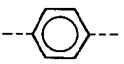
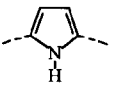
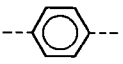
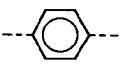
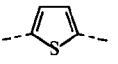
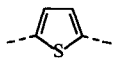
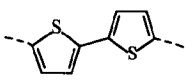
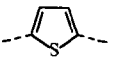
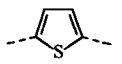
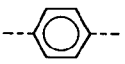
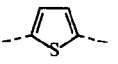
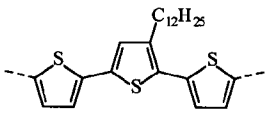
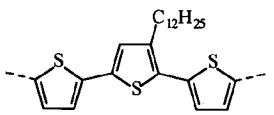
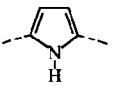
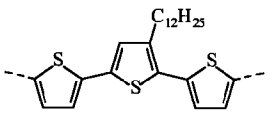
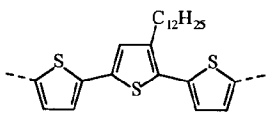
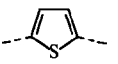
44 Andersson, M. R.; Pei, Q.; Hjertberg, T.; Inganäs, O.; Wennerström, O.; Österholm, J.-E. *Synth. Met.* **1993**, *55-57*, 1227

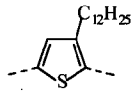
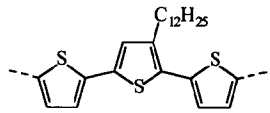
vibration intensity. Pyrroles were obtained upon the reaction with ammonia in an autoclave at 250°C (polymer **3.66**) or with ammonium acetate in dichlorobenzene (polymer **3.73**). The different polymers are outlined in table 3.2.



scheme 3.27 *AA-BB-Polymerization reaction.* (Ar, Ar' and Het are defined in table 3.2)

Table 3.2 *Polymers obtained by the AA-BB-polymerization*

Polyketone	Ar	Ar'	Polyarene	Het
3.65			**3.66**	
			**3.67**	
3.68			**3.69**	
3.70			**3.71**	
3.72			**3.73**	
			**3.74**	

3.75		

3.3.2 Characterization

Due to the insolubility of the compounds of table 3.2 (except polymer **3.75**), the most useful tool for the structural analysis is IR spectroscopy. Important absorptions are the carbonyl and the aromatic vibrations that are found in the region between 1600 cm^{-1} and 1700 cm^{-1} and between 700 cm^{-1} and 800 cm^{-1}, respectively. The intensive carbonyl vibrations are dependent on the type of aromatic ring attached to the carbonyl group. For the all-phenylene diketone **3.65** the absorption is found at 1680 cm^{-1}, whereas for the thiophene diketones **3.66** and **3.72** the signals are found at 1649 cm^{-1} and 1651 cm^{-1}, respectively. Mixed diketone **3.70** has two carbonyl signals at 1678 cm^{-1} and 1663 cm^{-1}. Proof of the polydiketone structures is obtained from the solid state NMR spectrum of poly-1,4-diketone **3.65** (figure 3.2). The ^{13}C-NMR spectrum clearly shows the expected

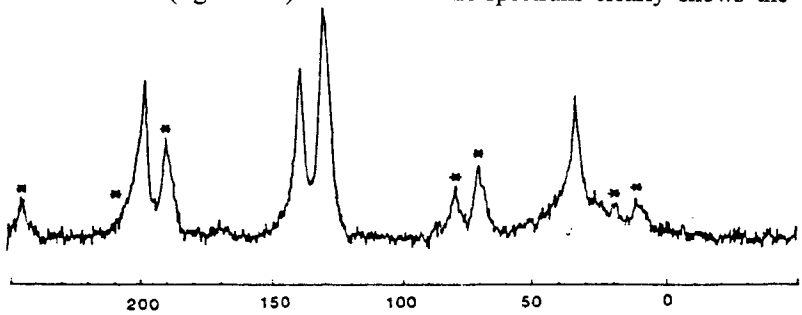


figure 3.2 *CP-MASS ^{13}C-NMR spectrum of polymer **3.65**.* (* denotes spinning side bands)

structure with four distinct carbon atoms, no end group resonances and a high degree of regularity. Of the polymers, only polyketone **3.75** is soluble. ^{1}H-NMR spectroscopy reveals the expected 1,4-diketone structure. In the aromatic region, signals are found at 7.2 and 7.7 ppm, arising from the ring protons without and with neighboring carbonyl groups, respectively. The diketone resonances are found at 3.3 to 3.4 ppm, comparable to oligomer diketones. For the alkyl side chains the benzylic signals are located at 2.8 ppm. However, the spectrum displays additional resonances at 3.0 ppm. These signals are thought to arise from non-1,4-diketone units (see figure 3.3), due to side reactions of the enone moieties similar to the polymerization of acrylates. The intensity of the signal is approximately 10

to 15 percent. Consequently, the polydiketone **3.75** has not been used in the cyclization reaction. Upon ring closure of the other poly-1,4-diketones, the carbonyl absorptions vanish and the aromatic absorptions become more intensive. This is especially noticed for the all-thiophene polymers **3.69** and **3.74**, which have a strong absorption at 789 cm^{-1} and 787 cm^{-1}, respectively. Copolymer **3.71** displays a similar effect with an absorption at 785 cm^{-1}. The polyaromatics are highly colored, ranging from dark brown to purple-black. Additionally, the dodecyl substituted polymers **3.73** and **3.74** have a green metallic luster.

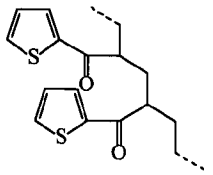


figure 3.3

Conductivities of the polyarenes were determined using four-point measurements. The measurements were preformed on pressed pellets after doping with iodine. Higher temperatures were required to ensure complete oxidation and the measurements were performed at the same temperatures to prevent de-doping due to evaporation of the dopant during the cooling process. The results are summarized in table 3.3. The highest conduc-

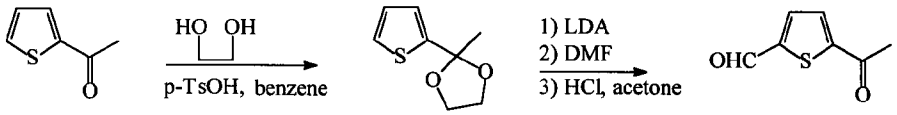
Table 3.3 *conductivities of polyarenes* (the numbers refer to table 3.2)

Polyarene	Conductivity ($S.cm^{-1}$)
3.66	0.14 (100 °C)
3.67	0.025 (100 °C)
3.69	0.02 (70 °C)
3.71	0.008 (70 °C)
3.73	0.5 (70 °C)
3.74	0.7 (70 °C)

tivities, 0.5 and 0.7 Scm^{-1}, are found for the dodecyl substituted polymers **3.73** and **3.74**, respectively. Although both polymers are insoluble, the solubilizing effect of the side chain results in a higher molecular weight of poly-1,4-diketone **3.72**, and the corresponding cyclization products have a greater conjugation length. Additionally, the side chain may induce some ordering in the materials. Consequently, the dodecyl substituted polymers display the highest conductivity. Polythiophene (**3.69**) displays a conductivity value of 0.02 Scm^{-1}, whereas copolymers **3.66** and **3.67**, although made up of only 50% heterocyclic rings, have higher values of 0.14 and 0.025 Scm^{-1}, respectively. These higher values are believed to arise from the higher temperature at which the measurements have been performed. A value of 0.008 Scm^{-1} for polymer **3.71** is in agreement with a low content of heterocyclic rings in the material, and a corresponding low amount of charge carriers.

3.3.3 AB-Polymerization

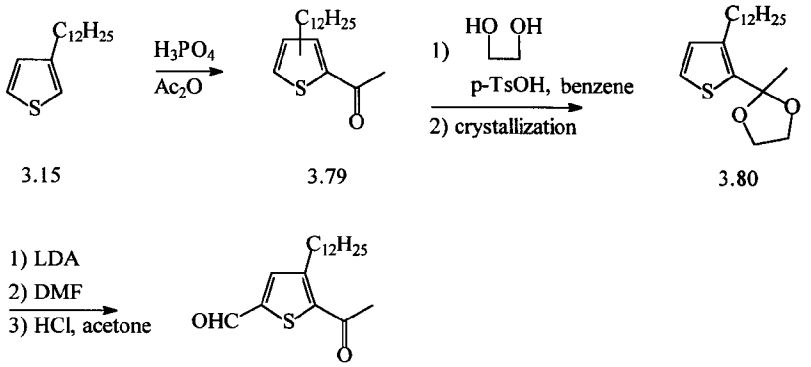
Alternatively, polydiketones can be synthesized using monomers containing both a donor and an acceptor moiety. These kinds of monomers have the advantage of an inherent equimolar distribution of the two reactants in the polymerization reaction. Thus, 2-acetylthiophene (**3.76**) was protected as the glycol ketal **3.77**, deprotonated and the anion quenched with DMF affording after hydrolysis 5-acetyl-thiophene-2-carbaldehyde (**3.78**)[44] (scheme 3.28). 3-Dodecylthiophene (**3.15**) was acylated affording a mixture of both 2- and



3.76 3.77 3.78

scheme 3.28

5-acetyl-3-dodecylthiophene (**3.79**). Protection with ethylene glycol and crystallization afforded the 2,3-isomer **3.80** in 35% yield (from **3.15**), which was converted to 5-acetyl-4-dodecyl-thiophene-2-carbaldehyde (**3.81**) by formylation and hydrolysis in 42% as outlined in scheme 3.29. The Mannich base of this compound should give, after poly



3.15 3.79 3.80

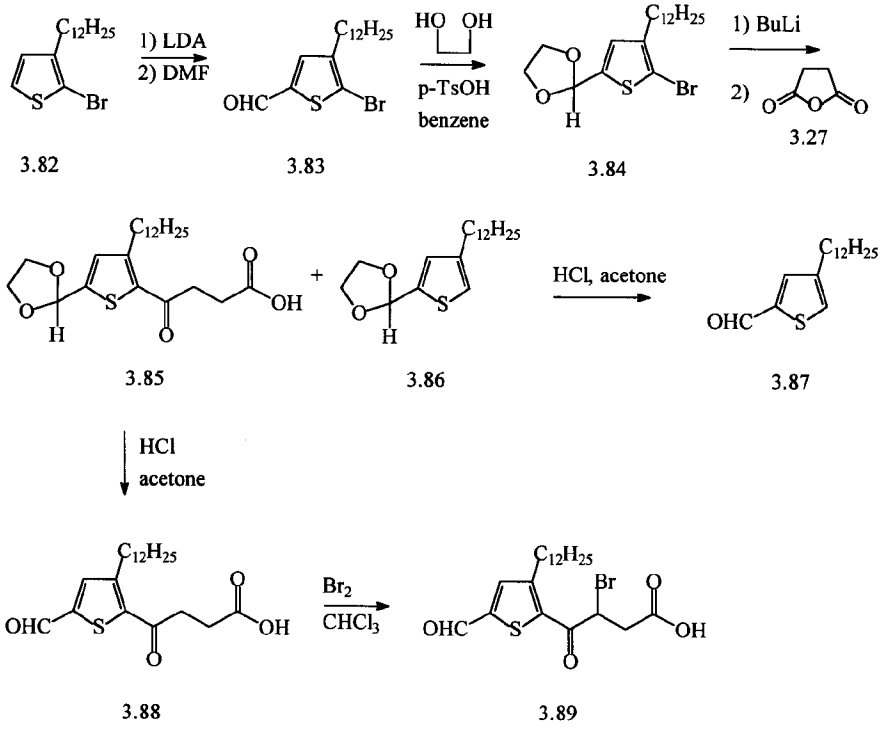
3.81

scheme 3.29

merization and ring closure, a substituted polythiophene with complete regioregularity. It turned out, however, that both compound **3.78** and **3.81** could not be transformed into the corresponding Mannich bases. We therefore decided to use unsaturated acid precursor **3.89**

44 Carpenter, A. J.; Chadwick, D. J. *Tetrahedron* **1985**, *41*, 3803

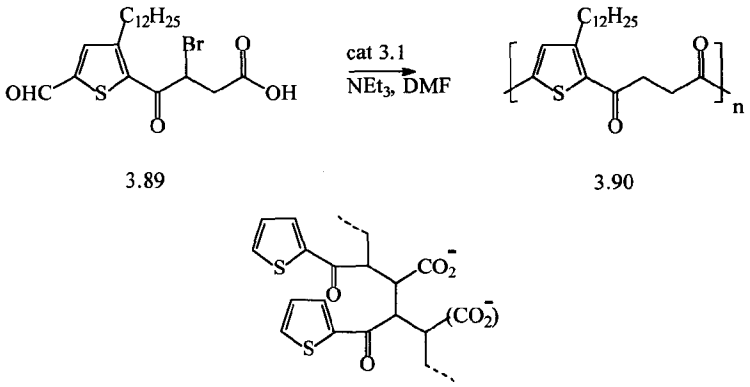
instead of the Mannich base. The synthesis is outlined in scheme 3.30. Thus, 2-bromo-3-dodecylthiophene (**3.82**) was deprotonated and the anion was quenched with DMF affording the aldehyde **3.83** in 91%. Aldehyde **3.83** was protected as the acetal **3.84** with ethylene glycol in a yield of 93%. Bromo lithium exchange with butyllithium afforded the anion, which was quenched with succinic anhydride (**3.27**), to afford acetal **3.85** in 42%. Besides **3.85** substantial amounts (up to 50%) of the debrominated compound **3.86** were obtained, which upon hydrolysis gave 4-dodecylthiophene-2-carbaldehyde(**3.87**). Acetal **3.85** was hydrolysed to 4-(3-dodecyl-5-formyl-thiophen-2-yl)-4-oxo-butyric acid (**3.88**). Bromination of **3.88** with bromine in chloroform afforded the precursor monomer **3.89** in



scheme 3.30

60% yield. The polymerization of **3.89** (scheme 3.31) was carried out with thiazolium salt **3.1** as catalyst and triethylamine as base. Triethylamine was used to deprotonate the thiazolium salt and the acid group, but also the induce the elimination of hydrogen bromide affording the double bond. Workup afforded a soluble product. ^{1}H-NMR displayed one signal in the aromatic region at 7.6 ppm, and the 1,4-diketone-CH_2 resonances at 3.4 ppm. However, the largest signal in the region between 2.4 and 3.6 ppm, was found at 3.0 ppm. Based on these NMR data, poly-1,4-diketone **3.90** appears to be contaminated with over 50% of moieties such as **3.91**, arising from reactions of acrylate functionalities. We

were not able to isolate the desired polyketone **3.90** from this mixture, and therefore, the reaction mixture was not used in the subsequent cyclization reaction.



3.89 3.90

3.91

scheme 3.31

3.3.4 Discussion

The polymerization of bis-Mannich bases and dialdehydes using the Stetter reaction is a powerful method for the synthesis of poly-1,4-diketones. Both the dialdehydes and diacetyl compounds are readily available. The bis-Mannich bases have been prepared by using dimethyl(methylene)ammonium chloride (**3.47**) or by the standard method with DMF as solvent to afford the products in good yields and in high purity (except for **3.53**). Introduction of a dodecyl side chain greatly influences the stability of the bis-Mannich compounds **3.59** and **3.62**. This decreased stability must be due to the dodecyl substituent because the unsubstituted Mannich compounds **3.53** and **3.56** are stable, with respect to storage and preparation. However, electronic effects cannot account for the decreased stability of the dodecyl substituted Mannich bases. Since alkyl groups are only slightly electron donating, the effect of the alkyl substituent will be compensated for by a second electron withdrawing carbonyl group in thiophene derivative **3.59**. It is more likely that the dodecyl substituents cause micelle formation of the Mannich bases. The resulting proximity of the amine functionalities causes the elimination of the amines and subsequent polymerization of the double bonds. The obtained polydiketones exhibit the expected structure as shown by IR and solid state ^{13}C-NMR spectroscopy. The fact that poly-1,4-diketone **3.75** is contaminated with non-1,4-diketone moieties, suggests that some structural defects may be present (particularly for the terthienyl derived polymers **3.72**, **3.73** and **3.74**). If

this is the case, however, the corresponding polythiophene would display the existence of these ketone moieties as well. Although these ketone functionalities are transformed into the thioketones during the cyclization reaction, the work-up procedure with NaOH will hydrolyse the thioketone groups, which normally are instable, back into the ketone functionalities. No ketone signals are found in IR, however, implying that the amount of non-1,4-diketone moieties is small. Upon ring closure with ammonia and Lawesson's reagent the 1,4-diketones units are converted to pyrrole rings and thiophene rings, respectively. Since the diketones are insoluble, this is a heterogeneous reaction, which requires high temperatures to accomplish complete ring closure. A possible side reaction could be furan formation, but upon heating the terthienyl diketone polymer in dichlorobenzene for 16 h, the diketone was recovered virtually unchanged. The conductivities of the polymers, although the values are lower than reported for substituted polythiophenes, confirm the structure of the materials. To put the values in perspective it is important to realize that the measurements were performed on pressed pellets. High conductivities are only obtained of thin films in the order of one to ten μm, whereas pressed pellets have thicknesses of a few hundred μm.

The synthesis of a polythiophene via the Stetter reaction using the A-B polymerization reaction failed, since the mono Mannich bases could not be prepared from the formyl acetyl thiophenes. A first explanation might be that the aldehyde moiety interferes with the Mannich reaction, but protection of the aldehyde as its ethylene glycol acetal did not afford the Mannich base, not when the reaction was carried out with dimethyl(methylene)ammonium chloride (**3.45**) nor when the anion of the acetyl functionality was quenched with **3.45**[45]. In the first case the acetal was recovered unchanged, while in the second case a mixture of unidentified products was obtained. Furthermore, the preparation of the Mannich base **3.7** proceeds even when an equivalent of thiophene-2-carbaldehyde (**3.6**) is added. From the fact, however, that quenching of the lithium derivative with **3.45** results in a complex reaction mixture, the conclusion can be drawn that the Mannich base is formed, but since it is derived as the free amine, it is not stable under these conditions. Attempts to protect the aldehyde of **3.78** by the formation of the dimeric benzoin, which can be used in the Stetter reaction directly, were unsuccessful. It turned out that the actual reaction that took place with NaCN was the Cannizzaro reaction, and the isolated product the corresponding ester. A good explanation for both effects is hard to give, since diacetyl compounds undergo the Mannich reaction and the dialdehydes can be used in the Stetter reaction, which requires the formation of a cyanohydrin species. Fur-

45 Danishefsky, S.; Kitahara, T.; McKee, R.; Schuda, P. F. *J. Am. Chem. Soc.* **1977**, *99*, 3028

thermore, aromatic dialdehydes have been polymerized via the benzoin condensation[46]. The synthesis of a monomer with the bromo acid precursor **3.89** as acceptor functionality, turned out to be more feasible, although the introduction of the keto acid moiety proceeded in low yields. This low yield stems from the low reactivity of succinic anhydride and is not due to the addition of a second equivalent of the lithium anion to the obtained keto acid as has been reported for the addition of lithium anions to phthalic anhydride[47]. Polymerization, however, did not afford the 1,4-diketone polymer with a satisfactory purity, because of the high reactivity of the unsaturated acid. The acrylate polymerization could not be suppressed using another base instead of triethylamine.

3.4 Concluding remarks

In this chapter we have described the synthesis of oligomers and polymers using the Stetter reaction. The reaction has proved to be very effective for the synthesis of oligomers with a large diversity of aromatic rings, introduced both in the diketone synthesis and the ring closure reactions. Side chains can be introduced readily, achieving solubility, but diminishing the conjugation length. Carboxylic esters, however, do not reduce the effective conjugation length.

Synthesis of polymers turned out to be more demanding, although the conversions in the diketone synthesis are high. The insolubility of the diketones prevents, to some extent, characterization and purification. With the introduction of side chains in the Mannich base, the resulting increase in reactivity is accompanied by side reactions. Ring closure reactions proceed in high yields, and although this heterogeneous reaction requires high temperatures, furan formation is negligible.

3.5 Experimental section

For general remarks, see section 2.4

The synthesis of compounds **3.15** and **3.60** has been described in chapter two. Compounds **3.7**[12], **3.13**[22] and **3.32**[29] were synthesized according to the literature procedures. UV spectra were recorded on a Perkin-Elmer Lambda 5 UV/VIS spectrophotometer. Conductivities were measured using a four probe method on pressed bars (20 x 5 x ~0.5 to 1 mm^3). Iodine doped samples were obtained by adding solid iodine to the bar and the measurements carried out at the temperature described in the text during the doping proces, until a constant

46 a) Wehr, R. **U.S. 3,419,462**: *C.A.* **1969**, *70*, 48193n. b) Kaul, S. N.; Fernanedz, J. E. *Macromolecules* **1987**, *20*, 2322

47 Parham, W. E.; Piccirilli, R. M. *J. Org. Chem.* **1976**, *41*, 1269

value was reached. The measurements were carried out at Philips Research Laboratories, Eindhoven under supervision of Dr. E. E. Havinga

3'-Dodecyl-[2,2';5',2'']-terthienyl (3.11)[35]

A mixture of 1,4-di-thiophen-2-yl-butane-1,4-dione (**3.8**) (20 g, 80 mmol), KOH (powdered, 22.5 g), n-dodecylbromide (40 g, 160 mmol) in DMSO (85 ml) was stirred for 2 days. The mixture was poured into water and extracted with toluene (3x200 ml). The organic layers were washed with water, brine and dried (Na_2SO_4). The solvent was removed and the residue dissolved in acetone (250 ml). 3N HCl (100 ml) was added and the mixture refluxed for 3 h. Most of the acetone was evaporated and the aqueous phase extracted with toluene (3x150 ml). The combined organic layers were washed with water, a $NaHCO_3$ solution, brine and dried (Na_2SO_4). The solvent was removed and the residue distilled (kugelrohr 130°C 0.1 mbar) taking of the excess dodecylbromide and the arisen dodecanol. The residue was dissolved in toluene (150 ml), Lawesson's reagent (25 g, 62 mmol) was added and the mixture refluxed for 2.5 h. The colored mixture was poured into 2N NaOH, the layers were separated and the aqueous phase extracted with toluene. The organic layers were washed with water, brine and dried (Na_2SO_4). Most of the solvent was removed, the residue dissolved in hexane, filtered over Al_2O_3, and distilled (kugelrohr). Crystallization from n-BuOH afforded 16.5 g (49%) of **3.11**. mp: 38.2-39.5°C (lit[35] 39-40°C). ^{1}H-NMR ($CDCl_3$) δ:0.91 (t, 3H), 1.28 (m, 18H), 1.67 (m, 2H), 2.74 (t, 2H), 7.03 (s, 1H), 7.05 (m, 2H), 7.16 (m, 2H), 7.21 (dd, 1H), 7.31 (dd, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:14.0 (q), 22.6 (t), 29.2 (t), 29.3 (t), 29.6 (t), 30.4 (t), 31.8 (t), 123.4 (d), 124.2 (d), 125.2 (d), 125.7 (d), 126.4 (d), 127.3 (d), 127.7 (d), 135.0 (s), 140.1 (d) ppm.

3'-Dodecyl-[2,2';5',2'']-terthienyl-5,5''-dicarbaldehyde (3.12)[21]

To DMF (40 ml), $POCl_3$ (11.3 ml) was added keeping the temperature below 30°C. To this mixture was added 3'-dodecyl-[2,2';5',2'']-terthienyl (**3.11**) (10.3 g, 25 mmol) and the temperature was brought to 100°C and remained at this temperature for 2 h, followed by 4 h at RT. The solid cake was poured into NaOH (35 g) in ice-water (250 ml) and left overnight. The mixture was extracted with toluene (5x100 ml). The organic layers were washed with water , brine and dried (Na_2SO_4). The volume was reduced, hexane added and the solution filtered over celite. Chromatography (Al_2O_3, toluene-hexane 1:1) and crystallization from MeOH afforded 6.1 g (52%) of **3.12** as yellow crystals. mp: 78.9-81.8°C. ^{1}H-NMR ($CDCl_3$) δ:0.88 (t, 3H), 1.26 (m, 18H), 1.69 (m, 2H), 2.81 (t, 2H), 7.22 (s, 1H), 7.27 (m, 2H), 7.69 (d, 1H), 7.73 (d, 1H), 9.88 (s, 1H), 9.90 (s, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:14.0 (q), 22.6 (t), 29.2 (t), 29.3 (t), 29.4 (t), 29.4 (t), 29.5 (t), 29.6 (t), 30.1 (t), 31.8 (t), 124.6 (d), 126.4 (d), 129.1 (d), 131.0 (s), 135.4 (s), 136.6 (d), 137.1 (d), 142.0 (s), 142.7 (s), 143.1 (s), 144.9 (s), 145.8 (s), 182.3 (d), 182.4 (d) ppm. HRMS calcd. for $C_{26}H_{32}O_2S_3$: 472.156, found: 472.156.

5,5''''-Diphenyl-3''-dodecyl-[2,2';5',2'';5'',2''';5''',2'''']-quinquethienyl (3.14)

A mixture of 3-dimethylamino-1-phenylpropan-1-one (**3.13**) (0.38 g, 2.15 mmol), 3'-dodecyl-[2,2';5',2'']-terthienyl-5,5''-dicarbaldehyde (**3.12**) (0.5 g, 1.06 mmol) and NaCN (10 mg) in DMF (15 ml) was stirred at RT for 2 days. The mixture was poured into water, acidified with HCl and extracted with CH_2Cl_2 (3x70 ml). The organic layers were washed with water, brine and dried (Na_2SO_4). The volume was reduced and the

solution filtered over Al_2O_3. The crude diketone obtained was dissolved in toluene (20 ml) after which Lawesson's reagent (1 g, 2.5 mmol) was added and the mixture refluxed for 2 h. After cooling and reduction of the volume the residue was filtered over Al_2O_3 and recrystallized from toluene. This gave 400 mg (51%) of **3.14** as an orange-red solid. mp: 172.5-175°C. ^{1}H-NMR ($CDCl_3$) δ:0.87 (t, 3H), 1.26 (m, 18H), 1.69 (m, 2H), 2.78 (t, 2H), 7.10 (m, 7H), 7.27 (m, 2H), 7.38 (m, 6H), 7.61, (d, 4H) ppm. UV($CHCl_3$) λ_{max}=429 nm. HRMS calcd. for $C_{44}H_{44}S_5$: 732.205, found: 732.205.

3-Dodecylthiophene-2,5-dicarbaldehyde (3.16)

To a solution of 3-dodecylthiophene (**3.15**) (13 g, 51.6 mmol) and TMEDA (15.6 ml, 104 mmol) in hexane (75 ml) was added n-BuLi (2.5 M, 45 ml). The mixture was stirred for 1 h at RT and refluxed for 45 min. After cooling to -60°C, THF (100 ml) was added to dissolve most of the white suspension and the solution was cooled to -80°C. DMF (25 ml) was then added and the mixture was allowed to reach RT. It was hydrolyzed with saturated NH_4Cl solution (100 ml) and extracted with ether (3x 100 ml). The combined organic layers were washed with water, brine and dried (Na_2SO_4). After evaporation of the solvents the residue was filtered over silica using hexane to remove the impurities and ether to give the product. Subsequent distillation (kugelrohr) afforded 13.7 g (86%) of **3.16** as an off-white semi solid. (bp: 200°C 0.05 mbar) ^{1}H-NMR ($CDCl_3$) δ:0.84 (t, 3H), 1.23 (m, 18H), 1.68 (m, 2H), 2.98 (t, 2H), 7.65 (s, 1H), 9.95 (s, 1H), 10.11 (s, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:13.9 (q), 22.5 (t), 28.3-29.4 (t), 31.1 (t), 31.7 (t), 137.0 (d), 143.0 (s), 147.6 (s), 151.8 (s), 182.7 (d), 183.1 (d) ppm. Anal. calcd. for $C_{18}H_{28}O_2S$: C 70.08, H 9.15, S 10.39, found: C 70.08, H 9.19, S 10.39.

3-Dodecyl-2,5-bis-(4-oxo-4-thiophen-2-yl-butyryl)-thiophene (3.18)

Na_2CO_3 (460 mg) was added to a solution of 4-oxo-4-thiophen-2-yl-but-2-enoic acid (**3.17**) (790 mg, 4.3 mmol, prepared according to the literature[24] with CH_2Cl_2 as solvent) in DMF (20 ml) and stirred for a 5 min. To this solution were added 3-dodecylthiophene-2,5-dicarbaldehyde (**3.16**) (650 mg, 2.1 mmol), catalyst **3.1** (40 mg) and NEt_3 (0.5 ml). The mixture was stirred at 80°C overnight and poured into cold diluted HCl and extracted with CH_2Cl_2 (2x100 ml). The combined organic layers were washed with water, brine and dried (Na_2SO_4). Evaporation of the solvents, chromatography (silica hexane-ether 1:1) and crystallization from 2-propanol afforded 540 mg (44%) of **3.18**. mp: 57.9-58.9 ^{1}H-NMR ($CDCl_3$) δ:0.87 (t, 3H), 1.25 (m, 18H), 2.97 (t, 2H), 3.38 (m, 8H), 7.15 (m, 2H), 7.65 (m, 3H), 7.81 (m, 2H) ppm. HRMS calcd. for $C_{32}H_{40}O_4S_3$: 584.209, found: 584.208.

3''-Dodecyl-[2,2';5',2'';5'',2''';5''',2'''']-quinquethienyl (3.19)

A mixture of tetraketone **3.18** (210 mg, 0.36 mmol) and Lawesson's reagent (600 mg, 2.4 mmol) in toluene (20 ml) was refluxed overnight. The highly colored solution was evaporated and chromatographed (silica, hexane) to give 130 mg (62%) of **3.19** as an orange solid.mp: 81.2-82.7°C ^{1}H-NMR ($CDCl_3$) δ:0.90 (t, 3H) 1.28 (m, 18H), 1.69 (m, 2H), 2.76 (t, 2H), 7.01-7.25 (m, 11H) ppm. UV($CHCl_3$) λ_{max}=407.5 nm. HRMS calcd. for $C_{32}H_{36}S_5$: 580.142, found: 580.142.

1,4-Bis-(hexyloxy)-benzene (3.21)

A mixture of hydroquinone (**3.20**) (15.0 g, 136 mmol), hexylbromide (47 g, 286 mmol), NaI (42 g), KOH (19 g) and EtOH (250 ml) was refluxed for 2 days. After cooling to 0°C, the dark colored product was collected on a glass filter and washed with plenty of water. The now slightly brown colored solid was recrystallized twice from EtOH to give 26.7 g (80%) of **3.21** as a white solid mp: 46.3-47.4°C. (lit[48]:39-40°C). ^{1}H-NMR ($CDCl_3$) δ:0.95 (t, 6H), 1.35 (m, 8H), 1.45 (m, 4H), 1.8 (quintet, 4H), 3.9 (t, 4H), 6.8 (s, 4H) ppm. ^{13}C-NMR ($CDCl_3$) δ:13.95 (q), 22.54 (t), 25.66 (t), 29.3 (t), 31.54 (t), 68.51 (t), 115.24 (d), 153.05 (s) ppm.

1,4-Dibromo-2,5-bis-(hexyloxy)-benzene (3.22)

To a solution of 1,4-bis-(hexyloxy)-benzene (**3.21**) (20,0 g, 74 mmol) in acetic acid (100 ml) and ether (10 ml) was added a solution of bromine (8 ml, 15 mmol) in acetic acid (20 ml). The mixture was stirred for 24 h and the solvents were evaporated. The resulting white solid was collected and recrystallized from ethanol to give 24 g (76%) **3.22**. mp: 63.0-64.1°C. ^{1}H-NMR ($CDCl_3$) δ:0.95 (t, 3H), 1.35 (m, 8H), 1.45 (m, 4H), 1.8 (quintet, 4H), 3.95 (t, 4H), 7.1 (s, 2H) ppm. ^{13}C-NMR ($CDCl_3$) δ:13.95 (q), 22.49 (t), 25.53 (t), 29.01 (t), 31.41 (t), 70.2 (t), 111.02 (s), 118.34 (d), 149.94 (s) ppm. Anal. calcd. for $C_{18}H_{28}Br_2O_2$: C 49.56, H 6.47, Br 36.63, found: C 49.77, H 6.54, Br 36.66, HRMS calcd. for $C_{18}H_{28}Br_2O_2$: 434.046, found: 434.047.

2,5-Bis-(hexyloxy)-terephthaldehyde (3.23)

1,4-Dibromo-2,5-bis-(hexyloxy)-benzene (**3.22**) (14.8 g, 34 mmol) in THF (80 ml) was added to a solution of n-BuLi (1.5 M, 50 ml) in 200 ml THF, keeping the temperature below -60°C. The temperature was allowed to raise to -40°C, resulting in a solid cake, hard to stir. The mixture was kept between -30 and -50°C for 1 h. It was then cooled to -80°C and dry DMF (10 ml, 130 mmol) was added. The cooling bath was removed, resulting in a clear, almost colorless solution at 10°C. Addition of NH_4Cl (100 ml 25%) gave a yellow organic layer that was separated. THF was removed and the residue dissolved in ether (100 ml). The aqueous layer was extracted with ether (2x50 ml) and the combined organic layers were washed with water, brine and dried ($MgSO_4$). After evaporation of the solvent, the product was recrystallized from 2-propanol giving 7.2 g (63%) of **3.23** as yellow crystals mp: 74.1-75.0°C. ^{1}H-NMR ($CDCl_3$) δ:0.95 (t, 6H), 1.35 (m, 8H), 1.45 (m, 4H), 1.8 (quintet, 4H), 4.0 (t, 4H), 7.4 (s, 2H), 10.45 (s, 2H) ppm. ^{13}C-NMR ($CDCl_3$) δ:13.58 (q), 22.40 (t), 25.54 (t), 28.87 (t), 31.31 (t), 69.04 (t), 111.40 (d), 129.04 (s), 154.98 (s), 189.11 (d) ppm. Anal. calcd. for $C_{20}H_{30}O_4$: C 71.82, H, 9.04, found: C 71.54, H 9.02, HRMS calcd. for $C_{20}H_{30}O_4$: 334.214, found: 334.215

1,4-Bis-(4-oxo-4-thiophen-2-yl-butyryl)-2,5-bis-(hexyloxy)-benzene (3.24)

A mixture of 4-oxo-4-thiophen-2-yl-but-2-enoic acid (**3.17**) (1.85 g, 10 mmol) and Na_2CO_3 (1.06 g, 10 mmol) in DMF (15 ml) were stirred for 15 min. After addition of 2,5-dihexyloxy-terephthaldehyde (**3.23**) (1.1 g, 3.3 mmol), catalyst **3.1** (400 mg) and NEt_3 (1 ml) the mixture was heated to 80°C and kept at that

48 Askari, S. H.; Rughooputh, S. D.; Wudl, F. *Synth. Met.* **1989**, *29*, E129

temperature overnight. The mixture was poured into cold diluted HCl and extracted with CH_2Cl_2 (2x100 ml). The organic phase was washed with water, a $NaHCO_3$ solution, brine and dried (Na_2SO_4). The solvent was evaporated and the residue chromatographed (silica, hexane-ether 1:1) to afford 1.2 g (61%) of **3.24** as a slightly yellow solid. mp: 94.4-96.5°C. ^{1}H-NMR ($CDCl_3$) δ:0.86 (t, 6H), 1.31 (m, 8H), 1.45 (m, 4H), 1.82 (quintet, 4H), 3.34 (t, 4H), 3.48 (t, 4H), 4.05 (t, 4H), 7.14 (dd, 2H), 7.35 (s, 2H), 7.63 (dd, 2H), 7.80 (dd, 2H) ppm. ^{13}C-NMR ($CDCl_3$) δ:13.8 (q), 22.4 (t), 25.6 (t), 29.0 (t), 31.3 (t), 33.5 (t), 38.1 (t), 69.1 (t), 114.1 (d), 127.9 (d), 130.8 (s), 131.7 (d), 133.2 (d), 143.8 (s), 151.9 (s), 191.5 (s), 199.9 (s) ppm. HRMS calcd. for $C_{34}H_{42}O_6S_2$: 610.242, found: 610.242.

1,4-Bis-([2,2']-bithiophen-5-yl)-2,5-bis-(hexyloxy)-benzene (3.25)

Tetraketone **3.24** (100 mg, 0.16 mmol) was dissolved in toluene (15 ml) and an excess of Lawesson's reagent (0.5 g) was added. The mixture was refluxed overnight giving a highly colored solution. The solvent was removed and the residue chromatographed (silica, hexane) and crystallized from 2-propanol. This afforded 85 mg (86%) of **3.25** as orange crystals mp: 150.2-152.4°C. ^{1}H-NMR ($CDCl_3$) δ: 0.94 (t, 6H), 1.41 (m, 8H), 1.59 (m, 4H), 1.94 (quintet, 4H), 4.11 (t, 4H), 7.05 (dd, 2H), 7.18 (d, 2H), 7.23 (m, 6H), 7.47 (d, 2H) ppm. ^{13}C-NMR ($CDCl_3$) δ:14.0 (q), 22.5 (t), 25.9 (t), 29.3 (t), 31.6 (t), 69.6 (t), 111.7 (d), 122.5 (s), 123.1 (d), 123.4 (d), 124.0 (d), 125.6 (d), 127.7 (d), 137.1 (s), 137.7 (s), 138.0 (s), 149.1 (s) ppm. UV($CHCl_3$) λ_{max}=404.4 nm. HRMS calcd. for $C_{34}H_{38}O_2S_4$: 606.175, found: 606.175.

1,4-Bis-(5-thiophen-2-yl-1H-pyrrol-2-yl)-2,5-bis-(hexyloxy)-benzene (3.26)

A solution of tetraketone **3.24** (200 mg, 0.33 mmol) and NH_4OAc (1 g) in HOAc (25 ml) was refluxed for 16 h. The dark colored mixture was cooled and poured into 200 ml water and extracted with CH_2Cl_2 (3x100 ml). The combined organic layers were washed with water, a $NaHCO_3$ solution, brine and dried (Na_2SO_4). The solvent was evaporated and the residue chromatographed (silica, ether). This afforded 140 mg (75%) of **3.26** as a rapidly colorizing solid. ^{1}H-NMR ($CDCl_3$) δ:0.91 (t, 6H), 1.38 (m, 8H), 1.58 (m, 4H), 1.98 (m, 4H), 4.11 (b, 4H), 6.49 (b, 2H), 6.60 (b, 2H), 7.17 (m, 8H), 10.24 (s, 2H) ppm. UV($CHCl_3$) λ_{max}=405.1 nm. oxidized 550 nm. HRMS calcd. for $C_{34}H_{40}N_2O_2S_2$: 572.253, found: 572.253.

3-Chlorocarbonyl-propionic acid dodecyl ester (3.28)

A mixture of n-dodecanol (8.6 g, 43 mmol) and succinic anhydride (**3.27**) (4.6 g, 43 mmol) in xylene (15 ml) was refluxed overnight. The xylene was evaporated and the residue crystallized from hexane giving 6.1 g (50%) of succinic acid monododecyl ester as a white solid. mp:47.4-49.4°C (lit[49]: 47.0-7.2°C). This was converted to the acid chloride by refluxing it for 3 h in $SOCl_2$ (25 ml). The solvent was evaporated and the residue distilled (kugelrohr, 180°C, 1 mm Hg). The acid chloride **3.28**, 5.8 g (90%) was obtained as a solidifying oil. ^{1}H-NMR ($CDCl_3$) δ:0.83 (t, 3H), 1.23 (m, 18H), 1.58 (m, 2H), 2.62 (t, 2H), 3.16 (t, 2H), 4.05 (t, 2H) ppm.

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49 Southern, J. A.; Riddle, C. D. *Furman Univ. Bull., Furman Studies* **1961**, *8*, 6: *C.A.* **1961**, *55*, 17131e

4-Oxo-4-thiophen-2-yl-butyric acid dodecyl ester (3.29)

To a solution of **3.28** (6.2 g, 20 mmol) and thiophene (1.9 g, 23 mmol) in CH_2Cl_2 (50 ml) was added $SnCl_4$ (2.5 ml, 21 mmol). The dark mixture was stirred at RT for 3.5 h, poured into diluted HCl and the layers separated. The organic layer was washed with water and dried. After the solvent was removed the residue was crystallized from hexane to give 5.2 g (74%) of **3.29** as an off white solid. mp: 34.3-35.6°C.^{1}H-NMR ($CDCl_3$) δ:0.87 (t, 3H), 1.25 (m, 18H), 1.60 (m, 2H), 2.75 (t, 2H), 3.24 (t, 2H), 4.07 (t, 2H), 7.12 (dd, J=5.1 Hz, J=3.8 Hz, 1H), 7.63 (dd, J=5.1 Hz, J=1.3 Hz, 1H), 7.75 (dd, J=3.8 Hz, J=0.9 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:14.0 (q), 22.5 (t), 25.7 (t), 28.1 (t), 28.4 (t), 29.1 (t), 29.2 (t), 29.4 (t), 29.4 (t), 29.5 (t), 31.8 (t), 33.8 (t), 64.8 (t), 127.9 (d), 131.8 (d), 133.4 (d), 143.5 (s), 172,6 (s) ppm.

3-Bromo-4-oxo-4-thiophen-2-yl-butyric acid dodecyl ester (3.30)

To a solution of 4-oxo-4-thiophen-2-yl-butyric acid dodecyl ester (**3.29**) (4 g, 11.4 mmol) in (50 ml) $CHCl_3$ was added 0.5 ml of a solution of bromine (1.83 g, 11.5 mmol) in $CHCl_3$ (5 ml). The reaction mixture was refluxed to start the reaction and after the bromine color had disappeared the rest of the bromine solution was slowly added. The mixture was stirred for another hour at RT and poured into water. The layers were separated and the aqueous layer extracted with 50 ml $CHCl_3$. The combined organic layers were washed with water (3x100 ml), brine and dried (Na_2SO_4). Evaporation of the solvent and crystallization from hexane gave 4.1 g (83%) of **3.30**. mp:32.3-32.8°C. ^{1}H-NMR ($CDCl_3$) δ:0.87 (t, 3H), 1.24 (m, 18H), 1.57 (m, 2H), 3.06 (dd, J=17.1 Hz, J=5.6 Hz, 1H), 4.61 (dd, J=17.1 Hz, J=9.0 Hz, 1H), 4.07 (m, 2H), 5.35 (dd, J=9.0 Hz, J=5.6 Hz, 1H), 7.17 (dd, J=4.7 Hz, J=3.8 Hz, 1H), 7.71 (dd, J=4.7 Hz, J=1.3 Hz, 1H), 7.87 (dd, J=3.8 Hz, J=1.3 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:13.9 (q), 22.5 (t), 25.7 (t), 28.3 (t), 29.0 (t), 29.2 (t), 29.3 (t), 29.4 (t), 29.5 (t), 31.8 (t), 38.5 (t), 40.1 (d), 65.3 (t), 128.2 (d), 133.2 (d), 135.0 (d), 140.5 (s), 169.9 (s), 185.4 (s) ppm.

[2,2';5',2'']-Terthiophene-4'-carboxylic acid dodecyl ester (3.31)

A mixture of of the bromide **3.30** (1.6 g, 3.7 mmol), thiophene-2-carbaldehyde (**3.6**) (420 mg, 3.8 mmol), catalyst **3.1** (100 mg, 0.4 mmol) in DMF (30 ml) was heated to 90°C, NEt_3 (1.5 ml) was added, and the reaction was kept at 90°C overnight. It was poured into cold diluted HCl and extracted with ether (3x100 ml). The organic phase was washed with water, brine (2x100 ml) and dried (Na_2SO_4). Chromatography (silica, hexane-ether 1:1) afforded 1 g (59%) of the diketone as a colored oil of 90% purity (based on ^{1}H-NMR). ^{1}H-NMR ($CDCl_3$) δ:0.85 (t, 3H), 1.29 (m, 18H), 1.52 (m, 2H), 3.67 (d, 2H), 4.08 (t, 2H), 4.92 (t, 1H), 7.12 (m, 2H), 7.62 (d, 1H), 7.68 (d, 1H), 7.79 (d, 1H), 7.94 (d, 1H) ppm.

The crude diketone (1 g), Lawesson's reagent (700 mg, 1.78 mmol) and toluene (50 ml) were heated at 80°C for 1 h and refluxed for another 2.5. The toluene was removed and the residue chromatographed (silica, hexane-ether 3:1) giving 740 mg (74%) of **3.31** as a rapidly colorizing oil. ^{1}H-NMR ($CDCl_3$) δ:0.88 (t, 3H), 1.25 (m, 18H), 1.72 (m, 2H), 4.27 (t, 2H), 7.07 (m, 2H), 7.21 (m, 1H), 7.27 (m, 1H), 7.40 (m, 2H), 7.52 (s, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:13.1 (q), 21.6 (t), 24.9 (t), 27.5 (t), 28.2 (t), 28.3 (t), 28.4 (t), 28.6 (t), 30.8 (t), 64.0 (t), 124.3 (d), 124.2 (d), 125.1 (d), 126.0 (d), 126.7 (d), 126.9 (d), 127.3 (s), 128.2 (d), 132.5 (s), 134.2 (s), 134.7 (s), 140.2 (s), 161.8 (s) ppm. HRMS calcd. for $C_{25}H_{32}O_2S_3$: 460.156, found: 460.156.

5,5'-Bis-(2-dodecyloxycarbonyl-4-oxo-4-thiophen-2-yl-butyryl)-[2,2']-bithienyl (3.33)

A mixture of [2,2']-bithienyl-5,5'-dicarbaldehyde (**3.32**) (160 mg, 0.72 mmol), bromide **3.30** (640 mg, 1.5 mmol), catalyst **3.1** (20 mg) in DMF (10 ml) was heated to 80°C. NEt_3 (0.5 ml) was added and the mixture kept at 80°C for 4 days. It was poured into cold diluted HCl and extracted with ether (3x100 ml). The organic layers were washed with water, brine and dried (Na_2SO_4). The solvents were removed and the crude material chromatographed (silica, hexane-ether 1:1). Crystallization from 2-propanol afforded 585 mg (88%) of **3.33** as a slightly colored solid. mp: 136-138°C. ^{1}H-NMR ($CDCl_3$) δ:0.87 (t, 6H), 1.21 (m, 36H), 1.56 (m, 4H), 3.72 (d, 4H), 4.11 (t, 4H), 4.91 (t, 2H), 7.15 (dd, 2H), 7.36 (d, 2H), 7.66 (dd, 2H), 7.83 (dd, 2H), 7.90 (d, 2H) ppm. ^{13}C-NMR ($CDCl_3$) δ:13.1 (q), 21.7 (t), 24.7 (t), 28.3 (t), 28.1 (t), 28.3 (t), 28.5 (t), 28.6 (t), 30.9 (t), 37.2 (t), 48.7 (d), 65.2 (t), 125.3 (d), 127.2 (d), 131.6 (d), 133.2 (d), 133.5 (d), 141.0 (s), 141.1 (s), 143.7 (s), 167.4 (s), 185.5 (s) ppm.

[2,2';5',2'';5'',2''';5''',2'''';5'''',2''''']-Sexithiophene-4',3''''-dicarboxylic acid didodecyl ester (3.34)

A mixture of tetraketone **3.33** (180 mg, 0.2 mmol) and Lawesson's reagent (200 mg, 0.5 mmol) in toluene (20 ml) was refluxed for 2.5 h. The mixture was cooled, poured into a $NaHCO_3$ solution and extracted with ether (3x50 ml). The combined organic layers were washed with water, brine and dried (Na_2SO_4). The solvents were evaporated, the residue chromatographed (silica, pentane-ether 20:1) and crystallized from hexane. This gave 60 mg (34%) of **3.34** as dark-red micro-crystals. mp: 105.4-106.6°C. ^{1}H-NMR ($CDCl_3$) δ: δ:0.86 (t, 6H), 1.24 (m, 32H), 1.72 (m, 4H), 4.28 (t, 4H), 7.04 (m, 2H), 7.18 (d, 2H), 7.25 (m, 4H), 7.43 (d, 2H), 7.53 (s, 2H) ppm. UV ($CHCl_3$) λmax 434.4 nm. Anal. calcd. for $C_{50}H_{62}O_4S_6$: C 65.32, H 6.80, S 20.93, found: C 65.49, H 6.83, S 21.20.

p-Hexyloxy-benzaldehyde (3.36)

A mixture of p-hydroxy benzaldehyde (**3.35**) (15 g, 123 mmol), n-hexylbromide (20.3 g, 124 mmol), KOH - pellets (85%, 8.1 g) and NaI (18 g) in 96% EtOH (150 ml) was refluxed for 18 h. The solvent was evaporated and water was added. The aqueous phase was extracted with ether (3x100 ml), the organic layers were combined, washed with water, brine and dried ($MgSO_4$). Evaporation of the solvent and distillation gave 18.4 g (72%) of **3.36** as a colorless oil bp 127-130°C 0.7 mm Hg (lit[50]. 154-155°C 6 mm Hg)

1,4-Bis-[3-(4-hexyloxy-phenyl)-acryloyl]-benzene (3.38)

p-Hexyloxy-benzaldehyde (**3.36**) (7.35 g, 36 mmol) and 1,4-diacetyl benzene (**3.37**) (2.9 g, 18 mmol) were dissolved in boiling EtOH (100 ml). To the still hot solution 40% NaOH (1 ml) was added. In a few min, stirring became impossible and after 15 min. the mixture was poured into diluted HCl (100 ml). The obtained dark yellow solid was isolated and recrystallized from $CHCl_3$ giving 4.2 g (45%) of **3.38** as yellow

50 Beilstein's "*Handbuch der Organischen Chemie*" **8**, III, 224

crystals. mp 198.9-199.4°C. ^{1}H-NMR ($CDCl_3$) δ:0.90 (t, 6H), 1.45 (m, 12H), 1.79 (quintet, 4H), 4.00 (t, 4H), 6.91 (d, J=8.5 Hz, 4H), 7.35 (d, J=15.6 Hz, 2H), 7.57 (d, J=8.5 Hz, 4H), 7.77 (d, J=15.6 Hz, 2H), 8.06 (s, 4H) ppm. ^{13}C-NMR ($CDCl_3$) δ:13.8 (q), 22.4 (t), 25.6 (t), 29.1 (t), 31.3 (t), 68.3 (t), 115.1 (d), 119.8 (d), 127.4 (s), 128.4 (d), 130.2 (d), 141.6 (s), 145.5 (d), 161.6 (s), 216.0 (s) ppm. Anal. calcd. for $C_{36}H_{42}O_4$: C 80.26, H 7.86, found: C 79.61, H 7.76.

1,4-Bis-[3-(4-hexyloxy-phenyl)-4-oxo-4-phenyl-butyryl]-benzene (3.40)

A mixture of chalcone **3.38** (1 g, 1.9 mmol), freshly distilled benzaldehyde (**3.39**) (500 mg), catalyst **3.1** (400 mg) and NEt_3 (0.5 ml) in DMF (40 ml) was stirred for 5 days at 80°C. The reaction mixture was poured into diluted HCl (100 ml) and extracted with $CHCl_3$ (3x100 ml). The combined organic layers were washed with water, a saturated $NaHCO_3$ solution, brine and dried. Evaporation of the solvents gave a dark oil which was filtered over deactivated Al_2O_3 with $CHCl_3$ and chromatographed (silica, ether) giving 100 mg (8%) of **3.40**. ^{1}H-NMR ($CDCl_3$) δ:0.86 (t, 6H), 1.17 (m, 8H), 1.29 (m, 4H), 1.71 (quintet, 4H), 3.24 (dd, 2H), 3.69 (t, 4H), 4.15 (dd, 2H), 5.23 (dd, 2H), 6.80 (d, 4H), 7.22 (d, 4H), 7.38 (m, 6H), 8.0 (m, 8H). ^{13}C-NMR ($CDCl_3$) δ:13.9 (q), 22.5 (t), 25.6 (t), 29.0 (t), 31.4 (t), 44.0 (t) 47.8 (d) 67.8 (t), 115.0 (d), 128.1 (d), 128.3 (d), 128.7 (d), 129.0 (d), 129.8 (s), 132.7 (d), 136.2 (s), 139.5 (s), 158.3 (s), 197.6 (s), 198.7 (s).

1,4-Bis-[4-(4-hexyloxy-phenyl)-5-phenyl-1H-pyrrol-2-yl] benzene (3.41)

A mixture of tetraketone **3.40** (90 mg, 0.1 mmol) and NH_4OAc (1 g) in HOAc (10 ml) was refluxed overnight. The resulting dark solution was cooled and poured into water and extracted with ether (3x50 ml). The organic layers were washed with water, a $NaHCO_3$ solution, brine and dried (Na_2SO_4). Evaporation of the solvent, chromatography (silica, ether/pentane) and recrystallization from ether/pentane afforded 40 mg (56%) of **3.41** as a solid. mp: 162.9-165.8°C. ^{1}H-NMR ($CDCl_3$) δ:0.95 (t, 6H), 1.38 (m, 8H), 1.50 (m, 4H), 1.81 (quintet, 4H), 3.98 (t, 4H), 6.69 (s, 2H), 6.88 (d, 4H), 7.35 (m,14), 5.58 (s, 4H), 8.43 (s, 2H). ^{13}C-NMR ($CDCl_3$) δ:14.0 (q), 22.6 (t), 25.7 (t), 29.2 (t), 31.6 (t), 67.9 (t), 108.5 (d), 114.3 (d), 123.7 (s), 124.0 (d), 126.7 (d), 127.2 (d), 128.5 (s), 128.6 (d), 129.3 (d), 129.7 (d), 130.0 (s), 131.7 (s), 133.0 (s). 157.5 (s).

1,4-Bispropionylbenzene (3.43)

Ethylbromide (30 g, 270 mmol) in ether (100 ml) was added to Mg (6.3 g, activated with iodine) at such a rate to maintain a gentle reflux. To the Grignard reagent terephthaldehyde (**3.41**) (11.6 g, 87 mmol) in THF (150 ml) was added with cooling. The resulting slightly green emulsion was stirred for another 30 min and poured into ice-water (600 ml) and H_2SO_4 (16 ml). The aqueous phase was extracted with ether (3x100 ml). The combined organic layers were washed with water, a saturated $NaHCO_3$ solution , brine and dried. The solvent was evaporated and the resulting oil dissolved in acetone (200 ml). The solution was cooled and Jones reagent[51] (81 ml) was added in 20 min. The acetone was evaporated and water and $NaHSO_3$ were added. The aqueous phase was extracted with CH_2Cl_2 (3x100 ml), the combined organic layers were washed

51 Vogel, A. I. *Textbook of practical organic chemistry* 4th Ed., Longman Inc. New York 1978 p 426

with water, brine and dried ($MgSO_4$). Evaporation of the solvent and recrystallization from EtOH gave 6.2 g (38%) of **3.43** as white crystals mp: 100.2-103.5°C. (lit[52] 100-102°C.) ^{1}H-NMR ($CDCl_3$) δ:1.25 (t, 6H), 3.05 (q, 4H), 8.05 (s, 4H) ppm. ^{13}C-NMR ($CDCl_3$) δ:8.0 (q), 32.0 (t), 128.1 (d), 139.7 (s), 199.8 (s) ppm.

1,4-Bis-(3-dimethylamino-2-methyl-propionyl)-benzene (3.44)

A mixture of **3.43** (5.4 g, 28.4 mmol), dimethylamine.HCl (5.1 g), 35% formaldehyde (5.5 ml) and HCl (conc, 1 ml) in EtOH (65 ml) was refluxed for 4 days. The resulting clear solution was poured into water (100 ml) and extracted with CH_2Cl_2 (2x100 ml). The aqueous phase was made alkaline with 0.1 M NaOH and extracted with CH_2Cl_2 (3x75 ml). The organic layers were washed with brine and dried (Na_2SO_4). Evaporation of the solvent afforded 2.5 g (29%) of **3.44** as a yellow semi solid. ^{1}H-NMR ($CDCl_3$) δ:1.95 (d, 6H), 2.26 (s, 12H), 2.37 (dd, 2H), 2.86 (m, 2H), 3.74, (m, 2H), 8.02 (s, 4H) ppm.

Attempted synthesis of **1,4-bis-(2-methyl-4-oxo-4-phenyl-butyryl)-benzene**

To a solution of **3.44** (900 mg, 3 mmol) and benzaldehyde (640 mg) in DMF (35 ml) was added NaCN (50 mg, 1 mmol), the mixture stirred at RT for 4 days, and poured into water (150 ml) and acidified with HCl. The resulting solid was collected and dried. This afforded (400 mg, 62%) of **1,4-bis-(2-methyl-acryloyl)-benzene (3.45)** as a white solid, mp 92.4-93.4°C. ^{1}H-NMR ($CDCl_3$) δ:2.05 (s, 6H), 5.63 (s, 2H), 5.96 (s, 2H), 7.72 (s, 4H) ppm. ^{13}C-NMR ($CDCl_3$) δ:18.3 (q), 128.1 (s), 128.8 (d), 140.4 (s), 143.5 (s), 197.4 (s) ppm.

Thiophene-2,5-dicarbaldehyde (3.46)[23]

To a mixture of thiophene (3.1 g, 37 mmol), TMEDA (11.1 ml, 74 mmol) in hexane (15 ml) was added n-Buli (1.6 M, 46 ml). This mixture was refluxed for 35 minutes, cooled below 0°C and after addition of THF (75 ml) to -60°C. DMF (7.4 ml) was than added and the temperature allowed to reach RT. The turbid mixture was poured into HCl/H_2O and extracted with CH_2Cl_2 (3x75 ml). The organic layers were combined and washed with water, a $NaHCO_3$ solution, brine and dried (Na_2SO_4). After evaporation of the solvent, the product was crystallized from water giving 3.5 g (71 %) of **3.46** as white crystals, mp: 116.3-117.3°C (lit[23]: 109-112.) ^{1}H-NMR ($CDCl_3$) δ:7.8 (s, 2H), 10.0 (s, 2H) ppm. ^{13}C-NMR ($CDCl_3$) δ:135.1 (d), 148.8 (s), 183.3 (d) ppm.

1,4-Bis-(3-dimethylaminopropionyl)-benzene (3.48)

A mixture of 1,4-diacetylbenzene (**3.37**) (3.2 g, 20 mmol) and dimethyl(methylene)ammonium chloride (**3.47**) (4.6 g, 50 mmol) in acetonitrile 50 ml was stirred at 30°C for 3h. After cooling to RT, the resulting solid was collected and recrystallized from EtOH/water. This afforded 5.8 g (84%) of **3.48**.2 HCl as a white

52 Beilstein's "*Handbuch der Organischen Chemie*" 7 IV 2168

solid. mp: 141-142.4°C (d). ^{1}H-NMR (D_2O) δ: 2.90 (s, 12H), 3.52 (t, 4H), 3.61 (t, 4H), 7.99 (s, 4H) ppm. ^{13}C-NMR (D_2O) δ: 36.0 (t), 45.6 (q), 55.2 (t), 131.1 (d), 141.7 (s) ppm. The free Mannich base was obtained by dissolving the salt in water, addition of ammonia and extraction with CH_2Cl_2 (3x70 ml). The organic layers were washed with water, brine and dried (Na_2SO_4). Evaporation of the solvent afforded the free base as a white solid. mp: 85-87°C.

Di-(2-ketopropyl)sulfide (3.50)[39]

A solution of $Na_2S.9H_2O$ (120 g, 0.5 mol) in H_2O (300 ml) was added in 50 min to a refluxing solution of chloroacetone (**3.49**) (93 g, 1 mol) in EtOH (450 ml). The mixture was refluxed for another 30 min and the EtOH evaporated. The aqueous phase was extracted with $CHCl_3$ (2x150 ml), the combined organic layers washed with water, brine and dried ($MgSO_4$). Evaporation of the solvent gave an orange oil which was dissolved in 150 ml EtOH. Cooling to -20°C gave 58 g (40%) of **3.50** as white crystals mp: 45.4-47.1°C. ^{1}H-NMR ($CDCl_3$) δ:2.3 (s, 6H), 3.4 (s, 4H) ppm. ^{13}C-NMR ($CDCl_3$) δ:28.1 (q), 41.4 (t), 202.4 (s) ppm.

2,5-Diacetylthiophene (3.52)[39]

A suspension of glyoxal trimer dihydrate (14.4 g) in ethanol (250 ml) was refluxed for 1 h affording monomeric glyoxal (**3.51**) and to the clear solution) of sulfide **3.50** (25 g, 171 mmol was added. To this solution a NaOEt solution (freshly prepared from Na (4.3 g) in EtOH (250 ml)) was added dropwise. The solvent was evaporated and water added. This dark colored mixture was extracted with $CHCl_3$ (2x150 ml). The organic layers were washed with water, brine and dried ($MgSO_4$). Evaporation of the solvent and chromatography (silica, CH_2Cl_2/pentane 1:1) gave 14.1 g (49%) of **3.52** as a slightly yellow solid, mp 170.1-172.6°C (lit[39]: 171.5-172°C) ^{1}H-NMR ($CDCl_3$) δ:2.5 (s, 6H), 7.7 (s, 2H) ppm. ^{13}C-NMR ($CDCl_3$) δ:26.9 (q), 131.9 (d), 148.9 (s), 190.7 (s) ppm.

[2,2']-Bithienyl (3.54)

To a solution of thiophene (16 ml, 200 mmol) in ether (100 ml) was added n-Buli (2.2 M, 90 ml) over a period of 0.5 h. After the spontaneous reflux had subsided, the mixture was stirred for an additional 0.5 h and coolded to -90°C. Anhydrous $CuCl_2$ (28 g, 208 mmol) was added at once, and the mixture was allowed to warm up. The temperature rose rapidly from -60°C to 0°C, and at RT the mixture was poured into cold diluted HCl (200 ml). The layers were seperated, and the aqueous phase extracted with ether (2x 100 ml). The combined organic layers were washed with water, brine and dried (Na_2SO_4). The solvent was evaporated and the residue distilled (kugelrohr, 90°C 1mm Hg). This afforded 10.1 g (76%) of **3.54** as a off-white solid. mp: 32-33°C. (lit: 33°C[53])

5,5'-Diacetyl-[2,2']-bithienyl (3.55)[40]

A mixture of [2,2']-bithienyl (**3.54**) (4.7 g, 28 mmol) in acetic anhydride (60 ml was heated to reflux, and 4 drops of H_3PO_4 (85%) were added. The resulting dark mixture was refluxed for an 1 h, poured into ice-

53 Steinkopf, W.; Leitsmann, R.; Hofmann, K. H. *Liebigs Ann. Chem.* **1937**, *546*, 180

water (300 ml) and extracted with CH_2Cl_2 (3 x 100 ml). The combined organic layers were washed with water, a $NaHCO_3$ solution, brine and dried (Na_2SO_4). Most of the solvent was evaporated and the residue filtered (silica, CH_2Cl_2). The resulting solid was recrystallized from dioxan to give 2 g (28%) of **3.55** as a yellow solid. mp: 230-232°C (lit[40] 233.5-234°C). The motherliqour contained the monoacylated derivative, which was purified by distillation (kugelrohr) to give 1.26 g (22%) of the monoacylated product.

5,5'-Bis-(3-dimethylaminopropionyl)-[2,2']-bithienyl (3.56)

A mixture of 5,5'-diacetyl-[2,2']-bithienyl (**3.55**) (1.6 g, 6.4 mmol), $NHMe_2$.HCl (1.05 g, 12.8 mmol), paraformaldehyde (385 mg) and HCl (conc, 0.3 ml) in DMF (200 ml) was stirred at 90°C for 6 h. After cooling to RT the solid was collected, washed with acetone and dried. This afforded 2.23 g (80%) of **3.56** as a yellow solid. The free Mannich base was obtained by dissolving the salt in water, addition of ammonia and extraction with CH_2Cl_2 (3x70 ml). The organic layers were washed with water, brine and dried (Na_2SO_4). ^{1}H-NMR ($CDCl_3$) δ:2.22 (s, 12H), 2.69 (t, 4H), 2.99 (t, 4H), 7.02 (d, 2H), 7.57 (d, 2H). ^{13}C-NMR ($CDCl_3$) δ:37.2 (t), 45.3 (q), 54.3 (t), 125.8 (d), 132.5 (d), 143.7 (s), 191.4 (s).

2,5-Dibromo-3-dodecylthiophene (3.57)

3-dodecylthiophene (**3.15**) (20 g, 80 mmol) was dissolved in a mixture of CH_2Cl_2 (50 ml) and HOAc (50 ml) and cooled to 15°C. Br_2 (25.6 g, 160 mmol) in HOAc (50 ml) was added and the reaction mixture was stirred at 15°C for two days. It was poured into H_2O (500 ml) and the layers separated. The aqueous layer was extracted with CH_2Cl_2 (3x150 ml) and the combined organic layers were washed with H_2O, a $NaHCO_3$ solution, H_2O and brine. Drying (Na_2SO_4), evaporation of the solvent and distillation (kugelrohr) gave 30 g (91%) of **3.57** as a colorless oil. (bp: 170°C 0.05 mbar) 1H-NMR ($CDCl_3$) δ:0.90 (t, 3H), 1.28 (m, 18H), 1.55 (m, 2H), 2.51 (t, 2H), 6.78 (s, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:14.2 (q), 22.7 (t), 28.9-29.7 (t), 31.9 (t), 107.9 (s), 110.3 (s), 130.9 (d), 142.9 (s) ppm. Anal. calcd. for $C_{16}H_{26}Br_2S$: C 46.84, H 6.39, Br 38.95, S 7.81, found: C 46.85, H 6.35, Br 38.98, S 7.82.

2,5-Diacetyl-3-dodecylthiophene (3.58)

A solution of 2,5-dibromo-3-dodecylthiophene **3.57** (10.2 g, 25 mmol) in THF (200 ml) was cooled to -40°C and to the white suspension n-BuLi (1.6 M, 32 ml) was added. The mixture was warmed up to -30°C giving a yellowish slurry and kept at this temperature for 30 min. After cooling to -60°C freshly prepared CuCl (5 g) was added. The mixture was warmed up to 0°C changing to dark yellow and clear. AcCl (5 ml) was added and at 15°C the mixture was poured into ice-water and extracted with hexane (4x75 ml). The combined organic layers were washed with H_2O, a $NaHCO_3$ solution, H_2O, brine and dried (Na_2SO_4). The solvents were evaporated and the residue crystallized from hexane (100 ml cooling to -25°C) and MeOH affording 5.2 g (63%) of **3.58** as a yellow solid. mp: 51.9-53.2°C ^{1}H-NMR ($CDCl_3$) δ:0.85 (t, 3H), 1.23 (m, 18H), 1.58 (m, 2H), 2.54 (s,3), 2.56 (s,3), 2.93 (t, 2H), 7.50 (s, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:14.0 (q), 22.5 (t), 26.8 (q), 29.2-30.1 (t), 29.7 (q), 31.8 (t), 134.9 (d), 140.8 (s), 144.7 (s), 150.4 (s), 190.8 (s), 191.3 (s) ppm. Anal. calcd. for $C_{20}H_{32}O_2S$: C 71.38, H 9.58, S 9.53, found: C 71.44, H 9.60, S 9.62.

5,5'-Diacetyl-3-dodecyl-[2,2']-bithienyl (3.61)

A mixture of 3-dodecyl-[2,2']-bithienyl (**3.60**) (5 g, 15 mmol), acetic anhydride (50 ml) and 85% H_3PO_4 (0.5 ml) was kept at 90°C for 3.5 h. The mixture was poured into H_2O (150 ml) and extracted with ether (3x100 ml). The combined organic layers were thoroughly washed with water, a $NaHCO_3$ solution, water, brine and dried (Na_2SO_4). the solvent was evaporated and the residue dissolved in hexane (75 ml). Cooling to -25°C gave 3.9 g of a yellow solid. This was chromatographed (silica) with hexane-ether (3:1) to give 300 mg of the mono acylated product[54] and hexane-ether (1:1) giving the product. Recrystallization from hexane afforded 3.4 g (54%) of **3.61** as yellow crystals, mp: 64-67.1°C. ^{1}H-NMR ($CDCl_3$) δ:0.84 (t, 3H), 1.24 (m, 18H), 1.62 (m, 2H) 2.53 (s, 3H) 2.56 (s, 3H), 2.76 (t, 2H), 7.2 (d, 1H), 7.49 (s, 1H), 7.61 (d, 2H) ppm. ^{13}C-NMR ($CDCl_3$) δ:13.9 (q), 22.5 (t), 26.4 (q), 29.1-29.4 (t), 30.1 (t), 31.7 (t), 127.4 (d), 132.5 (d), 134.8 (d), 137.8 (s), 141.9 (s), 142.1 (s), 143.1 (s), 144.4 (s), 190.1 (s), 190.2 (s) ppm. Anal. calcd. for $C_{24}H_{34}O_2S_2$: C 68.85, H 8.19, S 15.32, found: C 68.76, H 8.14, S 15.27.

5,5'-Bis-(3-dimethylamino-propionyl)-3-dodecyl-[2,2']-bithienyl (3.62)

To a mixture of 5,5'-diacetyl-3-dodecyl-[2,2']-bithienyl (**3.61**) (3 g, 7.2 mmol), dimethylamine.HCl (1.17 g, 14.4 mmol) and paraformaldehyde (431 mg, 14.4 mmol) in DMF (10 ml) was added 3 drops of HCl (conc). The solution was stirred at 70- 80°C overnight and cooled. The solid was collected and washed with ether and acetone yielding 1.7 g (40%) of **3.62** as an instable yellow solid. ^{1}H-NMR (D_2O) (all peaks are broad) δ:0.75, 1.15, 2.70, 3.20, 6.96, 7.22, 7.51 ppm.

5,5''-Diacetyl-3'-dodecyl-[2,2';5',2'']-terthienyl (3.63)

A solution of 3'-dodecyl-[2,2';5',2'']-terthienyl (**3.11**) (12 g, 29 mmol), acetic anhydride (7.5 g) and 85% H_3PO_4 (0.25 ml) was heated at 100°C for 1 h. The mixture was poured into water and extracted with CH_2Cl_2 (3x200 ml). The organic layers were washed with water, a $NaHCO_3$ solution, brine and dried (Na_2SO_4). The solvent was removed, the residue dissolved in MeOH and filtered over Al_2O_3. Chromatography (Al_2O_3, CH_2Cl_2) and crystallization from MeOH afforded 5 g (35%) of **3.63** as a yellow solid. mp: 90.4-90.8°C. ^{1}H-NMR ($CDCl_3$) δ:0.88 (t, 3H), 1.26 (m, 18H), 1.67 (m, 2H), 2.56 (s, 3H), 2.57 (s, 3H), 2.79 (t, 2H), 7.17 (m, 3H) 7.59 (d, 1H), 7.64 (d, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:14.0 (q), 22.6 (t), 26.4 (q), 26.5 (q), 29.2 (t), 29.3 (t), 29.4 (t), 29.4 (t), 29.5 (t), 30.1 (t), 31.8 (t), 124.3 (d), 126.3 (d), 128.5 (d), 130.7 (s), 132.6 (d), 133.1 (d), 142.4 (s), 142.6 (s), 143.3 (s), 143.7 (s), 144.6 (s), 190.0 (s), 190.2 (s) ppm. HRMS calcd. for $C_{28}H_{36}O_2S_3$: 500.188, found: 500.189.

5,5''-Bis-(3-dimethylamino-propionyl)-3'-dodecyl-[2,2';5',2'']-terthienyl (3.64)

A mixture of 5,5''-diacetyl-3'-dodecyl-2,2',5',2''-terthienyl (**3.63**) (3 g, 6 mmol), dimethylamine.HCl (1 g, 12.2 mmol), paraformaldehyde (380 mg, 12.2 mmol), HCl (conc, 0.5 ml) in DMF (50 ml) was heated at

54 The mono acylated product was formed as a 1:1 mixture of both isomers as shown by its ^{1}H-NMR spectrum; two acetyl resonances, a quartet for the benzylic protons arising from a double triplet and a complex pattern in the aromatic region.

100°C overnight. The mixture was cooled and the resulting solid was collected and washed with ether giving 2.9 g (70%) of **3.64** as a red solid. ^{1}H-NMR (MeOD) δ:0.63 (t, 3H), 1.01 (m, 18H), 1.40 (m, 2H), 2.54 (t, 2H), 2.71 (s, 12H), 3.05 (m, 8H), 7.05 (d, J=4.3 Hz, 1H), 7.08 (s, J=3.8 Hz, 1H), 7.11 (d, J=4.3 Hz, 1H), 7.67 (d, 1H), 7.21 (d, J=3.8 Hz, 1H) ppm. The free Mannich base was obtained by dissolving the salt in water, addition of ammonia and extraction with CH_2Cl_2 (3x70 ml). The organic layers were washed with water, brine and dried (Na_2SO_4). ^{1}H-NMR ($CDCl_3$) δ:0.87 (t, 3H), 1.26 (m, 18H), 1.67 (m, 2H), 2.29 (s, 12H), 2.77 (m, 6H), 3.07 (dt, 4H), 7.17 (m, 3H), 7.63 (d, 1H), 7.67 (d, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:14.0 (q), 22.6 (t), 29.2 (t), 29.3 (t), 29.4 (t), 29.5 (t), 30.2 (t), 31.8 (t), 37.2 (t), 37.3 (t), 45.3 (q), 54.2 (t), 124.3 (d), 126.3 (d), 128.6 (d), 130.8 (s), 132.1 (d), 132.6 (d), 135.3 (s), 142.5 (s), 143.2 (s), 143.7 (s), 144.6 (s), 191.4 (s), 191.6 (s) ppm.

Poly-1,4-(phenyl-1,4-diyl)butane-1,4-dione (3.65)

1,4-Bis-(3-dimethylaminopropionyl)-benzene (**3.48**) (5.4957 g, 21.513 mmol, freshly prepared from the hydrochloride salt) and terephthaldehyde (2.8856 g, 21.315 mmol, recrystallized from water) were dissolved in DMF (80 ml). To the solution was added sodium cyanide (200 mg) and the dark colored mixture was stirred at RT overnight. After the addition of more DMF (50 ml) the viscous reaction mixture was stirred at 55°C for two days, during which time the product precipitated, and poured into water (400 ml). The resulting solid was collected and was with water, EtOH, CH_2Cl_2 and ether and dried. This afforded 5 g (81%) of **3.65** as a yellow solid. mp: > 250°C. IR (KBr) cm^{-1}: 1680 (s), 841 (m). SS-^{13}C-NMR δ: 32.4 (t), 129.4 (d), 138.5 (s), 197.5 (s) ppm.

Poly-1,4-(1-H-pyrrol-2,5-diyl) phenylene (3.66)

Polyketone **3.65** (1.0 g) was heated with NH_3 in an autoclave for 16 h at 250°C and 9 bar. The apparatus was cooled and the NH_3 evaporated, affording **3.66** as a dark solid. IR (KBr) cm^{-1}: 1604 (m), 835 (m), 771 (m).

Poly-1,4-(thiophen-2,5-diyl)phenylene (3.67)

A mixture of polydiketone **3.65** (1.0 g), LR (2 g) and o-dichlorobenzene (30 ml) was refluxed for 2 days, and cooled. The resulting dark solid was collected and washed with EtOH, water and stirred overnight in 20% NaOH to remove last traces of LR. Washing with water, EtOH, $CHCl_3$ and acetone afforded 900 mg (90%) of **3.67** as a black solid. IR (KBr) cm^{-1}: 1595, (m), 832 (m).

Poly-5-(4-oxo-4-thiophene-2,5-diyl-butyryl)-5'-(4-oxo-butyryl)-[2,2']-bithienyl (3.68)

As described for **3.65** with dialdehyde **3.46** (202.9 mg, 1.4482 mmol), bis mannich base **3.56** (527.9 mg, 1.4482 mmol), NaCN (10 mg, 0.2 mmol) in DMF (30 ml) and 4 days at RT, affording 600 mg (95%) of **3.68**. IR (KBr) cm^{-1}: 1649 (s), 781 (m).

Poly(thiophen-2,5-diyl) (3.69)

As described for **3.67** with polydiketone **3.68** (450 mg), LR (1 g) in dichlorobenzene (50 ml). This afforded 400 mg (90%) of **3.69** as a dark brown-black colored solid. IR (KBr) cm^{-1}: 1026 (m), 789 (s).

Poly-1-(4-oxo-4-thiophene-2,5-diyl-butyryl)-4-(4-oxo-butyryl)phenylene (3.70)

As described for **3.65** with Mannich base **3.48** (1.1690 g, 5.4 mmol), dialdehyde **3.46** (757.2 mg, 5.4 mmol), NaCN (50 mg, 1 mmol) in DMF (30 ml), 3 days at RT and 1 night 70°C. Pouring into water gave an emulsion that upon the addition of HCl afforded 1.53 g (90%) **3.70** as a yellow brown solid. IR (KBr) cm^{-1}: 1678 (s), 1662 (s), 991 (w).

Poly-1,4-([2,2';5',2'']-terthiophen-5,5''-diyl)phenylene (3.71)

As described for **3.67** with polydiketone **3.70** (1.06 g), LR (2.5 g) and dichlorobenzene (100 ml). 60 h Reflux afforded 1 g (95%) of **3.71** as a brown solid. IR (KBr) cm^{-1}: 1659 (w), 1643 (w), 785 (s).

Poly-1,4-(3'-dodecyl-[2,2';5',2'']-terthiophen-5,5''-diyl)-butane-1,4-dione (3.72)

As described for **3.65** with dialdehyde **3.12** (2.1612 g, 4.572 mmol), Mannich base **3.64** (2.8115 g, 4.572 mmol), NaCN (40 mg, 0.8 mmol) in DMF (100 ml), 3 days at RT afforded 4.3 g (90%) of **3.70** as a red solid. IR (KBr) cm^{-1}: 2920 (s), 2849 (s), 1651 (s), 1435 (s), 1061 (m), 796 (m), 779 (m).

Poly-2,5-(3'-dodecyl-[2,2';5',2'']-terthiophen-5,5''-diyl)-1-H-pyrrole (3.73)

A mixture of polydiketone **3.72** (1 g), NH_4OAc (3 g) in dichlorobenzene (50 ml) was refluxed for 3 days. During the reaction NH_4OAc (1 g) was added daily (necessary due to the evaporation of some NH_3). The mixture was cooled, the solid collected and washed with EtOH and plenty of water, than again with EtOH and $CHCl_3$ affording 900 mg (90%) of **3.73** as a purple black solid with a green metallic luster. IR (KBr) cm^{-1}: 2918 (s), 2847 (s), 1578 (s), 1425 (s), 791 (s), 764 (s).

Poly-(3''-dodecyl-[2,2';5',2'';5'',2''']-quarthiophen-5,5'''-diyl) (3.74)

As described for **3.67** with polydiketone **3.72** (1 g), LR (2 g) in dichlorobenzene (50 ml) and 3 days reflux. This afforded 1 g of **3.74** as a purple black solid with a green metallic luster. The dichlorobenzene layer had a purple color (maximum 550 nm) but is after one reprecipitation from EtOH no longer soluble. IR (KBr) cm^{-1}: 2918 (s), 2849 (s), 1452 (m), 787 (s).

2-(Thiophen-2-yl)-2-methyl-[1,3]dioxolane (3.77)[44]

A mixture of 2-acetylthiophene (**3.76**) (35.5 g, 132 mmol), ethylene glycol (89 g), p-TsOH (150 mg) in benzene (300 ml) was refluxed. The reaction was monitored by ^{1}H-NMR and continued until the acetyl signal had disappeared. This required a reaction time of 4 days. The mixture was cooled, 5% NaOH (100 ml)

was added and the layers separated. The organic phase was washed with water, brine and dried (Na_2SO_4). Evaporation of the solvent and recrystallization from pentane afforded 35.9 g (75%) of **3.77** as a white solid. mp: 31-32°C (lit[44] 32-33°C).

5-Acetyl-thiophene-2-carbaldehyde (3.78)[44]

A solution of **3.77** (10 g, 59 mmol), n-BuLi (1.6 M, 40 ml), TMEDA (9 ml) in THF (350 ml) was stirred at -60°C for 3 h, cooled to -80°C and DMF (14 ml) was added. The mixture was allowed to reach RT over-night. Water (50 ml) was added and the THF evaporated. The aqueous phase was extracted with ether (4x50 ml) and the combined organic phases washed with brine and dried ($MgSO_4$). The solvent was evaporated and the oily residue stirred in HCl-water for 3 h. The resulting solid was collected and recrystallized from pentane-EtOAc, affording 8.3 g (91%) of **3.78** as a yellow solid. mp: 105.4-106.4°C (lit[44] 103-104°C)

2-(3-Dodecyl-thiophen-2-yl)-2-methyl-[1,3]dioxolane (3.80)

A mixture of 3-dodecylthiophene (**3.15**) (14 g, 56 mmol), 85% H_3PO_4 (1 ml) and acetic anhydride (80 ml) was kept at 70°C for 4.5 h. The resulting dark mixture was cooled to RT and poured into water and extracted with ether (3x150 ml). The combined organic layers were washed with water, a $NaHCO_3$ solution brine and dried (Na_2SO_4). The ether was evaporated and the crude compound, consisting of the 2- and the 5-acetyl-3-dodecylthiophene (**3.77**) was dissolved in benzene (150 ml). Ethylene glycol (10 ml) and p-TsOH (0.5 g) were added and the reaction mixture was refluxed overnight with azeotropic water removal by means of a Dean Stark trap. After cooling it was poured into a $NaHCO_3$ solution. The layers were separated and the aqueous phase extracted with ether (2x100 ml). The combined organic layers were washed with brine and dried (Na_2SO_4). Removal of the solvents and crystallization from hexane (cooling to -25°C) gave 6.6 g (35%) of **3.80** as a solid. ^{1}H-NMR ($CDCl_3$) δ:0.89 (t, 3H), 1.28 (m, 18H), 1.58 (m, 2H), 1.75 (s, 3H), 2.69 (t, 2H), 3.93 (m, 2H), 4.04 (m, 2H), 6.86 (d, 1H), 7.08 (d, 2H) ppm. ^{13}C-NMR ($CDCl_3$) δ:13.9 (q), 22.6 (t), 27.3 (q), 28.3 (t), 29.2 (t), 29.4 (t), 29.5 (t), 29.5 (t), 29.6 (t), 30.8 (t), 31.8 (t), 64.6 (s), 107.7 (s), 122.6 (d), 129.9 (d), 138.6 (s) ppm. The mother liquor mainly consisted of the other isomer that rapidly hydrolysed. ^{1}H-NMR ($CDCl_3$) δ:0.91 (t, 3H), 1.29 (m, 18H), 1.62 (m, 2H), 1.78 (s, 3H), 2.56 (t, 2H), 4.02 (m, 4H), 6.82 (s, 1H), 6.90 (s, 1H) ppm.

5-Acetyl-4-dodecyl-thiophene-2-carbaldehyde (3.81)

To a solution of LDA (16 mmol) in THF (60 ml) at -70°C was added of the ketal **3.80** (4.45 g, 13 mmol). The temperature was kept below -20°C for 2 h cooled to -70°C and DMF (2 ml) was added. The mixture allowed to reach RT, hydrolysed with a NH_4Cl solution and the layers were separated. The aqueous phase was extracted with ether (3x50 ml), the combined organic layers were washed with water, brine and dried (Na_2SO_4). The solvents were evaporated and the residue was dissolved in acetone (100 ml). After 2N HCl (100 ml) was added the mixture was refluxed for 3 h. The acetone was evaporated and ether (100 ml) was added. The layers were separated and the aqueous layer was extracted with ether (2x50 ml). The combined organic layers were washed with water, a $NaHCO_3$ solution, brine and dried (Na_2SO_4). The solvent was removed and the residue crystallized from hexane affording 1.75 g (42%) of **3.81** as a yellow solid. mp: 52-

53.7°C. ^{1}H-NMR ($CDCl_3$) δ:0.85 (t, 3H), 1.25 (m, 18H), 1.59 (m, 2H) 2.55 (s, 3H), 2.97 (t, 2H), 7.61 (s, 1H), 9.93 (s, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:13.9 (q), 22.5 (t), 29.2-29.9 (t), 29.7 (q), 138.1 (d), 141.4 (s), 143.7 (s), 150.2 (s), 183.3 (d), 191.4 (s) ppm. HRMS calcd. for $C_{19}H_{30}O_2S$: 322.197, found: 322.197.

5-Bromo-4-dodecyl-thiophene-2-carbaldehyde (3.83)

To a mixture of diisopropylamine (4 ml, 29 mmol) in THF (75 ml) at -20°C was added n-BuLi (2.5M, 11 ml). After cooling to -70°C 2-bromo-3-dodecylthiophene (**3.82**) (9 g, 27 mmol) was added and the mixture was kept between -70 and -40°C for 1.5 h. It was recooled to -75°C and DMF (4 ml) was added. The temperature was raised to -5°C and the reaction was quenched with a saturated NH_4Cl solution. The layers were separated and the aqueous phase extracted with ether (2x100 ml). The combined organic layers were washed with brine and dried (Na_2SO_4). Evaporation of the solvents gave 8.6 g (91%) of **3.83** of 95% purity (based on ^{1}H-NMR) which was used without further purification. ^{1}H-NMR ($CDCl_3$) δ:0.84 (t, 3H), 1.23 (m, 18H), 1.57 (m, 2H), 2.55 (t, 2H), 7.42 (s, 1H), 9.71 (s, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:13.9 (q), 22.5 (t), 28.9 (t), 29.1 (t), 29.2 (t), 29.3 (t), 29.4 (t), 31.7 (t), 121.7 (s), 136.5 (d), 143.7 (s), 181.4 (s) ppm.

2-(4-Dodecyl-5-bromo-thiophen-2-yl)-[1,3]dioxolane (3.84)

A mixture of aldehyde **3.83** (8.2 g, 23 mmol), ethyleneglycol (5 ml) and p-TsOH in benzene (70 ml) was refluxed overnight with azeotropic water removal by means of a Dean-Stark trap. The cooled mixture was poured into a $NaHCO_3$ solution and the layers were separated. The aqueous phase was extracted with ether (2x100 ml) and the combined organic layers were washed with water, brine and dried (Na_2SO_4). Removal of the solvents and crystallization from pentane with the aid of decolorizing charcoal afforded 8.5 g (93%) of **3.84** as white crystals. mp: 26.1-26.9°C. ^{1}H-NMR ($CDCl_3$) δ: 0.95 (t, 3H), 1.32 (m, 18H), 2.52 (t, 2H), 3.95 (m, 4H), 5.89 (s, 1H), 6.78 (s, 1H) ppm. HRMS calcd. for $C_{19}H_{31}BrO_2S$: 402.123, found: 402.123.

4-(5-[1,3]-Dioxolan-2-yl-3-dodecyl-thiophen-2-yl)-4-oxo-butyric acid (3.85)

To a solution of acetal **3.84** (2 g, 5 mmol) in THF (10 ml) at -70°C was added n-BuLi (2.5M, 2 ml) and the temperature raised to -40°C. The mixture was cooled to -50°C and added to a mixture of succinic anhydride (**3.27**) (2 g, 20 mmol) in THF (20 ml) at -100°C. The temperature was allowed to reach RT overnight and poured into a NH_4Cl solution. The layers were separated and the aqueous phase extracted with ether (3x100 ml). The combined organic layers were washed with brine and dried (Na_2SO_4). Evaporation of the solvents and chromatography of the residue (silica, $CHCl_3$-EtOAc 9:1) gave 0.9 g (42%) of **3.85** as an off white solid. ^{1}H-NMR ($CDCl_3$) δ:0.86 (t, 3H), 1.23 (m, 18H), 1.75 (m, 2H), 2.74 (t, 2H), 2.92 (t, 2H), 3.14 (t, 2H), 4.05 (m, 4H), 6.05 (s, 1H), 7.03 (s, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:13.9 (q), 22.5 (t), 27.9 (t), 29.1 (t), 29.3 (t), 29.4 (t), 29.9 (t), 30.3 (t), 31.7 (t), 35.7 (t), 65.1 (t), 99.6 (d), 129.7 (d), 134.3 (s), 145.9 (s), 150.7 (s), 178.5 (s), 190.9 (s) ppm.

Furthermore was isolated (with $CHCl_3$-pentane 1:1 as eluent) 2-(4-Dodecyl-thiophen-2-yl)-[1,3]dioxolane (**3.86**). ^{1}H-NMR ($CDCl_3$) δ:0.91 (t, 3H), 1.31 (m, 18H), 1.69 (m, 2H), 2.57 (t, 2H), 4.07 (m, 4H), 6.07 (s, 1H), 6.92 (s, 1H), 7.02 (s, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:13.9 (q), 22.5 (t), 29.1 (t), 29.2 (t), 29.3 (t), 29.5 (t),30.3 (t), 31.8 (t), 65.0 (t), 100.2 (d), 120.7 (d), 127.3 (d), 141.0 (s), 142.7 (s) ppm. HRMS calcd. for $C_{19}H_{32}O_2S$: 324.211, found: 324.212.

This compound easily hydrolysed to afford 4-dodecyl-thiophene-2-carbaldehyde (**3.87**). ^{1}H-NMR ($CDCl_3$) δ:0.85 (t, 3H), 1.25 (m, 18H), 1.60 (m, 2H), 2.61 (t, 2H), 7.34 (s, 1H), 7.56 (s, 1H), 9.83 (s, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:13.9 (q), 22.5 (t), 29.0 (t), 29.2 (t), 29.4 (t), 29.4 (t), 29.9 (t), 30.2 (t), 31.7 (t), 130.1 (d), 136.9 (d), 143.4 (s), 144.5 (s), 182.7 (d) ppm.

4-(3-Dodecyl-5-formyl-thiophen-2-yl)-4-oxo-butyric acid (3.88)

The acetal **3.85** was stirred in a water acetone HCl mixture for two h at RT. After most of the acetone was evaporated the aqueous phase was extracted with ether. The ether extracts were washed with water, brine and dried (Na_2SO_4). Evaporation of the solvent and crystallization from pentane gave **3.88** as a white solid. ^{1}H-NMR ($CDCl_3$) δ:0.85 (t, 3H), 1.23 (m, 18H), 1.56 (m, 2H), 2.78 (t, 2H), 2.97 (t, 2H), 3.20 (t, 2H), 7.67 (s, 1H), 9.93 (s, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:14.0 (q), 22.5 (t), 27.8 (t), 29.2 (t), 29.3 (t), 29.5 (t), 29.9 (t) 30.1 (t), 31.8 (t), 36.1 (t), 138.1 (d), 140.5 (s), 143.8 (s), 150.7 (s), 178.4 (s), 183.4 (d), 191.6 (s) ppm. HRMS calcd. for $C_{21}H_{32}O_4S$: 380.202, found: 380.202.

3-Bromo-4-(3-dodecyl-5-formyl-thiophen-2-yl)-4-oxo-butyric acid (3.89)

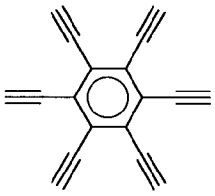
To a hot solution of of the keto acid **3.88** (750 mg, 2 mmol) in $CHCl_3$ (10 ml) was added 0.5 ml of a solution of Br_2 (400 mg) in $CHCl_3$ (40 ml). After the color had disappeared, the rest of the bromine solution was added. After the reaction was completed (1 h) the mixture was poured into water, the layers separated and the aqueous phase extracted with $CHCl_3$ (2x100 ml). The combined organic layers were washed with water (2x100 ml), brine and dried (Na_2SO_4). The solvent was evaporated and the oily residue treated with pentane giving 540 mg (60%) of **3.89** as an off white solid. mp 65.9-68.8°C. ^{1}H-NMR ($CDCl_3$) δ:0.89 (t, 3H), 1.25 (m, 18H), 1.61 (m, 2H), 2.99 (m, 2H), 3.08 (dd, J=17.5 Hz, J=4.7 Hz, 1H), 3.52 (dd, J=15.4 Hz, J=9.4 Hz, 1H), 5.13 (dd, J=9.4 Hz, J=5.1 Hz, 1H), 7.65 (s, 1H), 9.97 (s, 1H), 10.92 (b, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:14.0 (q), 22.5 (t), 29.2 (t), 29.3 (t), 29.4 (t), 29.5 (t), 29.8 (t), 30.2 (t), 31.8 (t), 38.1 (t), 41.5 (d), 137.6 (s), 137.9 (d), 144.6 (s), 153.3 (s), 175.7 (s), 183.3 (d), 186.3 (s) ppm. HRMS calcd. for $C_{21}H_{31}BrO_4S$: 458.113, found: no exact mass could be determined, due to elimination of HBr, as indicated by the M/e 380 peak in the mass spectrum.

Chapter four

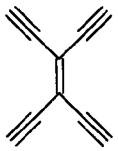
Design and synthesis of two-dimensional co-planar conjugated systems based on the pyrazine moiety

4:1 Introduction

The electrical properties of conjugated molecules depend on the mobility of charge carriers, both interchain (the hopping of charge carriers such as electrons) and intrachain. Small interchain distances and, hence, highly ordered (crystalline) materials are required to facilitate the hopping of charge carriers. Another approach to minimize the interchain distances and to reduce the influence of the hopping limitation is the synthesis of two- or even three-dimensional networks. The best example of a π-conjugated three-dimensional structure is graphite. Large conjugated all-carbon networks, other than graphite, are believed to exhibit metallic character[1] and interesting non-linear optical properties[2]. The synthesis of π-conjugated networks is very demanding, but due to the bright prospects, considerable effort has been directed towards the preparation of these systems. The new carbon allotropes are based on the acetylene moiety with hexaethynylbenzene (**4.1**) and tetraethynylethene (**4.2**) as most frequently applied building blocks or monomers[3] (figure 4.1).



4.1



4.2

figure 4.1

In this chapter we propose the pyrazine moiety as building block for the synthesis of two-dimensional structures. Since pyrazine is applicable in the synthesis of both one-dimensional and two-dimensional polymers through the use of pyrazine monomers containing two and four functionalities, respectively, it is a perfect synthon to investigate two-dimensional structures with well-defined model compounds. Alternatively, three-dimensional networks can be prepared by the crosslinking of linear polymers. Before discussing

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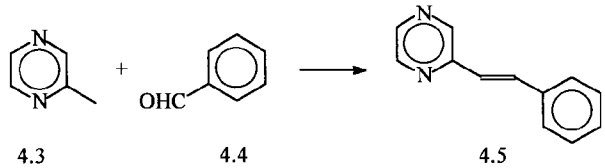
1 Hoffman, R.; Hughbanks, R.; Kertész, M.; Bird, P. H.; *J. Am. Chem. Soc.* **1983**, *105*, 4831
2 Baughman, R. H.; Eckhardt, H.; Kertész, M. *J. Chem. Phys.* **1987**, *87*, 6687
3 for a review, see: Diederich, F. *Nature* **1994**, *369*, 199

our approach, a short review on pyrazine chemistry is given here.

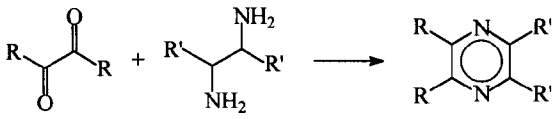
Methylpyrazines (**4.3**) as well as α-and γ-picolines possess relatively acidic methyl protons, which upon condensation with aromatic aldehydes (**4.4**) afford the corresponding styryl compounds (**4.5**) (scheme 4.1). The condensations have been carried out by using acid catalysis[4], including 3,5-dinitro benzoic acid[5], sulfuric acid[6] and zinc chloride[7]. Base catalysis has also been used, but only low yields have been reported[8].



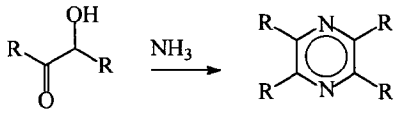
4.3 4.4 4.5

scheme 4.1

The condensation of 1,2-diketones (**4.6**) with 1,2-diamino compounds[9,10] (**4.7**) and that of α-hydroxy ketones (**4.9**) with ammonia[11] or ammonium acetate[12] are well-established methods for the synthesis of pyrazines (**4.8** or **4.10** respectively) (scheme 4.2), and a variety of methods for the synthesis of α-hydroxy ketones and 1,2-diketones



4.6 4.7 4.8



4.9 4.10

scheme 4.2

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4 Bennett, G. M.; Willis, G. H. *J. Chem. Soc.* **1928**, 1960.

5 Nethsinghe, P. L.; Plesch, P. H.; Hodge, D. J. *Angew. Makromol. Chem.* **1987**, *148*, 161.

6 a) LaTulip, R. J. **U.S. US 4,500,690**: *C.A.* **1985**, *102*, 204856t. b) Treybig, D. S. **U.S. US 4,613,663**: *C.A.* **1987**, *106*, 5946e.

7 a) Treybig, D. S.; Swearingen L. L. **U.S. US 4,543,388**: *C.A.* **1986**, *104*, 51594v. b) Teshirogi, T. **Jpn. Kokai Tokkyo Koho JP 01,113,375 [89,113,375]**: *C.A.* **1989**, *111*, 233858m.

8 Ried, W.; Hinsching, S. *Liebigs Ann. Chem.* **1956**, *600*, 47.

9 Bost, R. W.; Towell, E. E. *J. Am. Chem. Soc.* **1948**, *70*, 903.

10 Flament, I.; Stoll, M. *Helv. Chem. Acta* **1967**, *50*, 1754.

11 Wieleman, J.; Vinot, N.; Villadary, M. *Bull. Chim. Soc. France* **1965**, 3476.

12 Vinot, N.; Pinson, J. *Bull. Chim. Soc. France* **1968**, 49[illegible].

are available. α-Hydroxy ketones can be prepared by the oxidation of ketones (containing α-hydrogens)[13,14], or epoxides[15], from 1,2-diketones[16], and via the acyloin[17] and the benzoin[18] condensation. 1,2-Diketones can be prepared by the oxidation of benzoins[19], and by the condensation of biacetyl derivatives with aromatic aldehydes[20,21]

Materials with attractive electrical properties can only be obtained if the molecules are fully conjugated; therefore they must have a coplanar structure. In the case of tetraphenylpyrazine (**4.10**, R=phenyl), the ortho-protons of the phenyl ring experience a considerable steric interaction causing the rings to twist. This twist probably results in a propeller-like structure with a low degree of conjugation (figure 4.2) or in a linear conjugated structure with two rings in the plane of the pyrazine ring and the other two phenyl ring perpendicular to the pyrazine ring.. Therefore, the aromatic rings must be connected not directly, but by means of the sterically smaller, yet conjugated vinyl moiety. Due to this requirement, the only practical synthetic method for the preparation of these systems is the condensation of aldehydes with methylpyrazines[22].

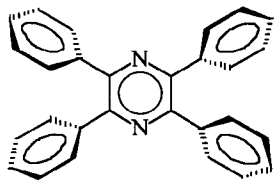

figure 4.2

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13 a) Vedejs, E.; Telschow, J. E.; *J. Org. Chem.* **1976**, *41*, 740. b) Rubottom, G. M.; Gruber, J. M. *J. Org. Chem.* **1978**, *43*, 1599.

14 Moriarty, R. M.; Hou, K. *Tetrahedron Lett.* **1984**, *25*, 691.

15 Santosusso, T. M.; Swern, D. *J. Org. Chem.* **1975**, *40*, 2764.

16 Kreiser, W. *Liebigs Ann. Chem.* **1971**, *745*, 164.

17 Bloomfield, J. J.; Owsley, D. C.; Nelke, J. M. *Org. React.* **1976**, *23*, 259.

18 Ide, W. S.; Buck, J. S. *Org. React.* **1948**, *4*, 269

19 Clarke, H. T.; Dreger, E. E. *Org. Synt.* Coll. Vol. **I**, 87.

20 Sörensen, N. A.; Samuelsen, E.; Oxaal, F. R. *Acta Chem. Scan.* **1947**, *1*, 458.

21 Shevchuk, M. I.; Kushnir, V. N.; Dombrovskii, V. A.; Khalaturnik, M. V.; Dombrovskii, A. V. *Zhurnal Obshchei Khimii* **1975**, *45*, 1228. Translation in English.

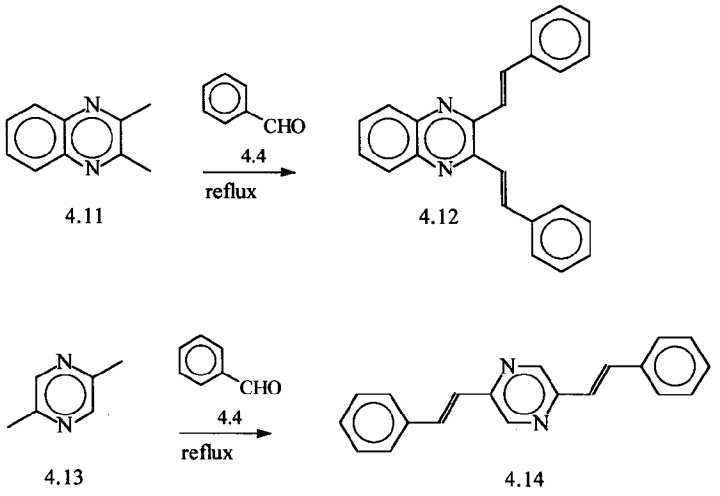
22 For the synthesis of two-dimensional polymers via the cross-linking of hydroxy ketones or diketones, it is necessary that in the precursor polymers the ketone moieties and the aromatic ring must be connected by the vinyl group. Synthesis of these kind of polyhydroxy ketones will fail using either the benzoin or the acyloin condensation reactions, since both reactions with cinnamyl derivatives do not give the hydroxy ketones (see Morton, A. A.; Stevens, J. R. *J. Chem. Soc.* **1930**, 2031 for the benzoin condensation and reference 17 for the acyloin condensation). Attempts to use TMSCl in the acyloin condensation of ethyl cinnamate, although mentioned (see reference 17) as an option to suppress the Dieckmann condensation, were unsuccessful.
Synthesis of the dimeric epoxide of cinnamaldehyde succeeded (see Mark, V. *Org. Synth.* Coll. Vol. **V**, 358), but subsequent oxidation did not afford the hydroxyketone (see reference 15 for the oxidation reaction). The condensation of biacetyl with benzaldehyde affords the diketone only in a yield of ten percent (see reference 20). Consequently, the synthesis of conjugated pyrazine networks is not feasible via the cyclization reaction of poly-α-hydroxy ketones or poly-1,2-diketones.

In this chapter we will investigate the scope and limitations of the pyrazine molecule as central building block. The synthesis of conjugated two-dimensional oligomers containing the pyrazine moiety, via an improved acid catalyzed method is reported. To obtain a good insight into the influence of this two-dimensionality with respect to the effective conjugation length a number of one-dimensional compounds has been synthesized as well.

4.2 Synthesis of one-dimensional systems

4.2.1 Model compounds

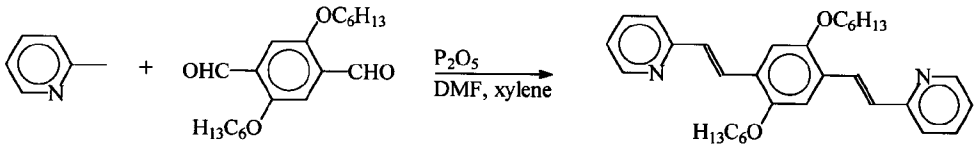
To determine the optimal reaction conditions for the condensation reaction, we set out with the synthesis of a number of linearly conjugated compounds containing the pyrazine moiety or its mono nitrogen equivalent, the pyridine ring. The syntheses were carried out by the condensation of dimethylpyrazine derivatives and 2-picoline with different aromatic mono- and dialdehydes, respectively. The condensation of 2,3-dimethyl quinoxaline (**4.11**), synthesized by the condensation of 1,2-diaminobenzene with biacetyl in acetic acid[9], with benzaldehyde (**4.4**) afforded 2,3-distyryl quinoxaline (**4.12**) in 54% yield (scheme 4.3). Benzaldehyde was used as reagent and solvent, but the reaction only



scheme 4.3

proceeded when crude benzaldehyde, containing some benzoic acid, was used. Analogously, 2,5-distyrylpyrazine (**4.14**) was obtained from benzaldehyde and 2,5-dimethylpyrazine (**4.13**) in 50% yield. Both products were obtained as yellow solids, with an all-

trans double bond configuration. Compound **4.14** is highly fluorescent, but very sensitive towards UV-radiation. Upon exposure to light, the color changes from yellow to white and the compound becomes insoluble in organic solvents such as DMF and $CHCl_3$. This change arises from the [2+2] photocycloaddition, which affords a polymer[23]. Although the condensation proceeds well, using the aldehyde as reagent and solvent, this method is not applicable when substituted (di)aldehydes are used, since their boiling points are too high, nor is it suitable for the synthesis of polymers. In these cases, both a solvent and catalyst are required. We used P_2O_5 as acid catalyst and dehydrating agent and a mixture of DMF and 5-10% xylene as solvent. P_2O_5 is acidic, (that is upon reaction with water, and the actual catalyst therefore, is phosphoric acid), has good dehydrating capabilities and is not an oxidant (unlike e.g. sulfuric acid). Furthermore, it is easily removed from the reaction mixture during workup. DMF is used because of its powerful solvating properties although it has a tendency to degenerate upon prolonged boiling. Therefore, xylene, which has a boiling point just below that of DMF, is added as co-solvent to prevent this. Thus, the reaction of 2,5-dihexyloxy terephthaldehyde (**4.16**) and 2-picoline (**4.15**) under the influence of P_2O_5 in a mixture of DMF and 10% xylene afforded 2,5-bis-hexyloxy-1,4-bis-(2-pyridin-2-yl-vinyl)-benzene (**4.17**) in an isolated yield of 35% (scheme 4.4).

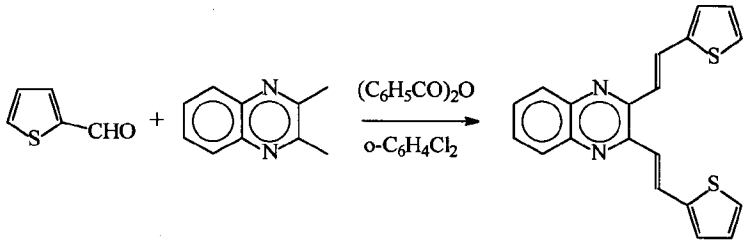


4.15 4.16 4.17

scheme 4.4

Extending the method to other aromatic aldehydes we used thiophene-2-carbaldehyde (**4.19**). It turned out, however, that the condensation with 2,3-dimethyl quinoxaline (**4.11**) failed when using the methods described previously; both with the solvent-free and the P_2O_5-DMF method only unidentified degradation products were obtained. Therefore, we used benzoic anhydride as dehydrating agent[23] to afford benzoic acid. The latter is used as catalyst and o-dichlorobenzene as solvent; this high boiling solvent has good solubility capacities and is relatively inert. Thus, reflux of a mixture of 2,3-dimethyl quinoxaline (**4.11**), the aldehyde **4.18** and crude (containing some acid) benzoic anhydride in o-dichlorobenzene gave a mixture of 2,3-bis-(2-thiophen-2-yl-vinyl)

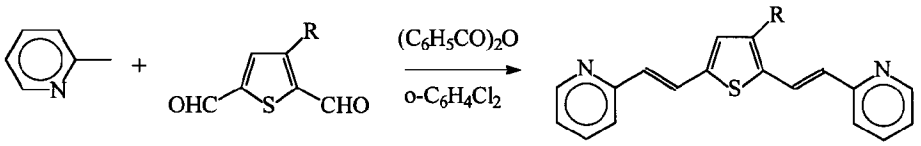
23 a) Hasegawa, M.; Suzuki, Y.; Suzuki, F.; Nakanishi, H. *J. Polym. Sci. Part A-1* **1969**, *7*, 743 b) Hasegawa, M.; Kinbara, K.; Adegawa, Y.; Saigo, K. *J. Am. Chem. Soc.* **1993**, *115*, 3820



4.18 4.12 4.19

scheme 4.5

quinoxaline (**4.19**) and 2-(2-thiophen-2-yl-vinyl)-3-methyl quinoxaline. Both compounds were readily separated by column chromatography (scheme 4.5). Crystallization afforded the compounds in 22% and 33% yield, respectively. Using the same reaction conditions, 2-picoline (**4.15**) was condensed with thiophene-2,5-dicarbaldehyde (**4.20**) and 3-dodecyl-thiophene-2,5-dicarbaldehyde (**4.22**), to provide 2,5-bis-(2-pyridin-2-yl-vinyl)-thiophene



4.15 4.20 (R=H) 4.21 (R=H)

4.22 ($R=C_{12}H_{25}$) 4.23 ($R=C_{12}H_{25}$)

scheme 4.6

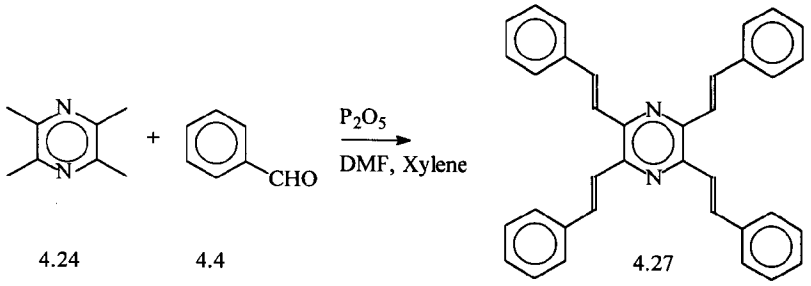
(**4.21**) and 3-dodecyl-2,5-bis-(2-pyridin-2-yl-vinyl)-thiophene (**4.23**), respectively. The large difference in reactivity of the two dialdehydes is remarkable. Compound **4.21** is obtained in an isolated yield of only 6%, after a reaction time of 9 days, whereas the substituted dialdehyde affords the product **4.23** in 30% yield in 3 days. The isolated yields of the condensation products described above are only moderate, although the conversions are higher. The condensation of the dialdehydes and dimethylpyrazine, therefore, will produce only low molecular weight materials. Consequently, the synthesis of linear polymers was not further investigated.

4.3 Synthesis of two-dimensional systems

For the preparation of two-dimensional compounds we have used the tetra-substituted pyrazine moiety as branching unit. The syntheses have been carried out by the condensation of tetramethylpyrazine with different aldehydes.

4.3.1 Model compounds

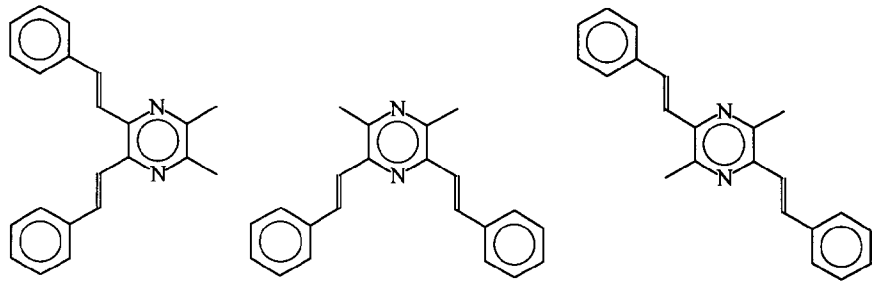
The model compounds were synthesized by the condensation of tetramethylpyrazine with benzaldehyde and thiophene-2-carbaldehyde respectively. Condensation of benzaldehyde (**4.4**) and tetramethylpyrazine (**4.24**) was carried out using the P_2O_5-DMF method, with a reaction time of 6 days. The crude reaction mixture consisted of the distyryl **4.25**, tristyryl **4.26** and tetrastyryl **4.27** compounds. Separation by column chromatography and subsequent crystallization afforded the isolated compounds **4.25**, **4.26** and **4.27** in 12%, 4% and 13% yield, respectively (scheme 4.7). The distryryl compound



4.24 4.4 4.27

scheme 4.7

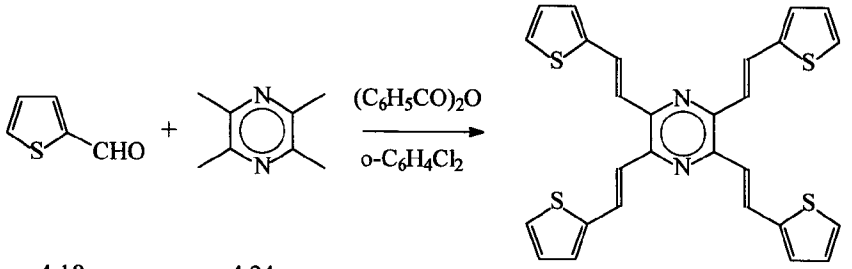
consisted of only one of the three possible isomers (**4.25a**, **4.25b** and **4.25c**). Of the three compounds, **4.25b** is not conjugated through the pyrazine ring, as is 2,6-distyrylpyridine having a λ_{max} of 338 nm[5]. Since **4.25** has a λ_{max} of 390 nm, **a** and **c** are the two possibilities left. NOESY analysis clearly showed an interaction between the methyl group and the double bond protons, indicating that the actual structure is **4.25c**. For the reaction



4.25a 4.25b 4.25c

of thiophene-2-carbaldehyde (**4.18**) and tetramethylpyrazine (**4.24**), benzoic anhydride was used as catalyst in dichlorobenzene as the solvent. This afforded 2,3,5,6-tetrakis-(2-

thiophen-2-yl-vinyl)-pyrazine (**4.28**) together with the tri- and di-substituted compounds. The products were obtained after a reaction time of six days in isolated yields of 3%, 11% and 12%, respectively. (scheme 4.8) The compounds, although obtained in high purity, were sensitive toward light and air.

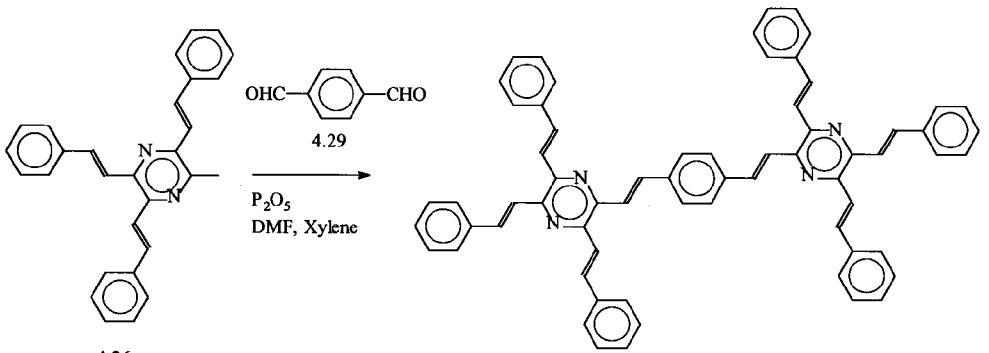


4.18 4.24 4.28

scheme 4.8

4.3.2 Oligomers

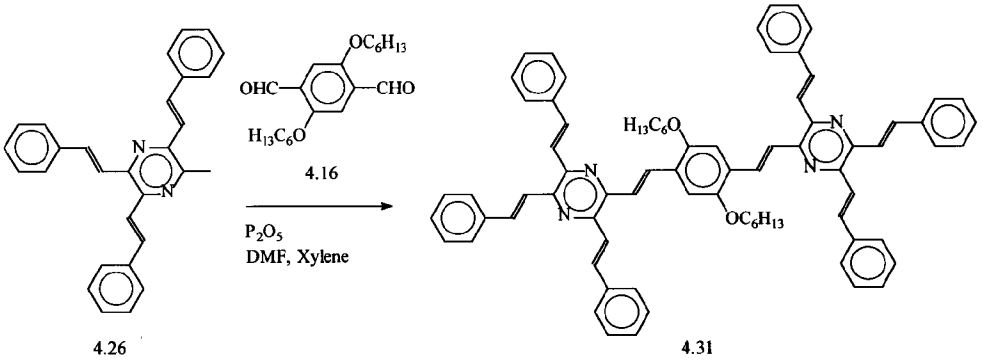
Since the model compounds can be obtained in high purity via the methods described, a logical extension was made to the synthesis of oligomers. The by-products in the preparation of the model compounds, especially the monomethylpyrazine derivatives, offer very suitable starting materials, which upon condensation with dialdehydes will give well-defined oligomers. The condensation of 2,3,5-tristyryl-6-methylpyrazine (**4.26**) and terephthaldehyde (**4.29**) afforded 1,4-bis-[2-(3,5,6-tristyryl-pyrazin-2-yl)-vinyl]-benzene (**4.30**) in 44% yield (scheme 4.9). The compound, dark red colored, was almost completely insoluble in common organic solvents like chloroform and toluene. IR and UV spectrosco-



4.26 4.30

scheme 4.9

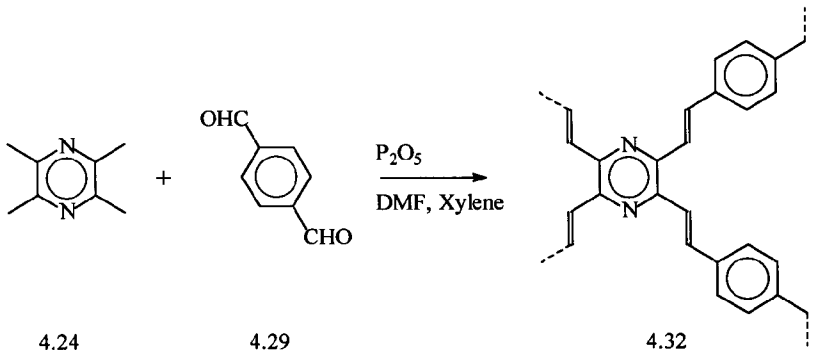
py, however, confirmed the assigned structure. To facilitate the characterization, 2,5-dihexyloxy-terephthaldehyde (**4.16**) was used. This afforded upon condensation with 2,3,5-tristyryl-6-methylpyrazine (**4.26**) 2,5-bis-hexyloxy-1,4-bis-[2-(3,5,6-tristyryl-pyrazin-2-yl)-vinyl]-benzene (**4.31**) in a yield of 15%. (scheme 4.10) The deep red colored compound was still sparingly soluble, but the solubility was sufficient to allow structural proof by ^{1}H-NMR spectroscopy.



scheme 4.10

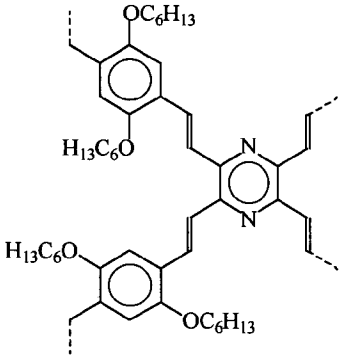
4.3.3 Polymers

Whereas for the synthesis of linear polymers high conversions are required, for the synthesis of polymer networks moderate conversions are sufficient to obtain high molecular weight materials. Furthermore, high conversions give rise to very high molecular weight polymers, which will presumably lead to insolubility and related problems. There-

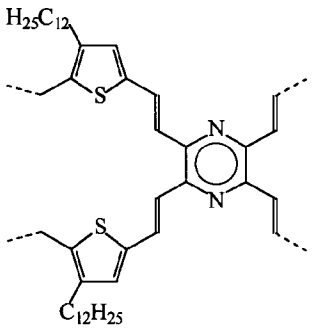


scheme 4.11

fore, the reaction conditions used for the synthesis of both model compounds and oligomers are suitable for the synthesis of two-dimensional polymers. The condensation of tetramethylpyrazine (**4.24**) with two equivalents terephthaldehyde (**4.29**) using the P_2O_5-DMF method afforded polymer **4.32** as an insoluble red material in 111% yield (scheme 4.11). This is based on a yield of 100% for the complete conversion of all the methyl and aldehyde functionalities. This implies that considerable amounts of unreacted aldehyde and methyl groups are still present in the material. The product precipitated from the reaction mixture during the reaction. Due to this insolubility, characterization of compound **4.32** can only be accomplished by IR spectroscopy. A comparison of the IR spectrum with that of the compounds described in the previous section strongly suggests that **4.32** has the structure depicted in scheme 4.11. Soluble polymer **4.33** was obtained in 69% yield from the reaction of tetramethylpyrazine (**4.24**) and two equivalents 2,5-dihexyloxy terephthaldehyde (**4.16**) using the same reaction conditions as used for the synthesis of **4.32**. The reaction of tetramethylpyrazine (**4.24**) and two equivalents 3-dodecyl thiophene-2,5-dicarbaldehyde (**4.22**) using benzoic anhydride as catalyst and dehydrating agent in dichlorobenzene afforded polymer **4.34** in 85% yield.



4.33



4.34

4.4 Characterization

A detailed characterization of the compounds prepared is required. Beside establishing their chemical purity and configuration of the double bonds, the pyrazine derivatives have been investigated with respect to the coplanarity of the systems. The absence of coplanarity is detrimental for interesting opto-electronic properties. NMR-spectroscopy has been carried out to establish the configuration of the double bonds present in almost all compounds prepared. The coupling constants in ^{1}H-NMR determined for the double bond protons are all approximately 15-16 Hz. This value is indicative of the all-trans configura-

tion. Oligomer **4.30** is virtually insoluble, which hampers an adequate characterization. However, IR spectroscopy showed the absence of any carbonyl vibration, in agreement with the structure assigned. Despite the two side chains, compound **4.31** is still only sparingly soluble, however, the structure could be confirmed by ^{1}H-NMR-spectroscopy. Although the complexity of the aromatic region hampers a correct assignment of the signals, the ^{1}H-spectrum clearly demonstrates the existence of four different double bonds.

Polymer **4.32** is, as might be expected, completely insoluble in all organic solvents including dichlorobenzene and DMF. IR spectrometry, the main tool for its characterization, indicated the expected structure (the vinyl vibration at 1624 cm^{-1}, also present in model compound **4.27** at 1624 cm^{-1} and oligomer **4.30** at 1627 cm^{-1}). There are, however, significant amounts of aldehyde (the carbonyl vibration at 1663 cm^{-1}) and methyl end groups present as well. Additional proof for the assigned structure is the red appearance of the material. The molecular weight of the soluble polymers **4.33** and **4.34** has been determined with GPC relative to polystyrene standards. Polymer **4.33** has a molecular weight of 2200 $g.mol^{-1}$, which is only approximately twice that of oligomer **4.31**. The vinyl vibration is found at 1616 cm^{-1}, but the intensity is weak, and considerable amounts of end-group vibrations are present as well. ^{1}H-NMR spectroscopy displays a very complex pattern, with both the aromatic and the vinyl resonances between approximately δ=6.8 and 8 ppm. Furthermore, a clear signal for the methyl end group is found at δ=2.6 ppm. Polymer **4.34** on the other hand, is considerably more polymer-like but consists of two different molecular weight fractions (denominated a and b). For the low molecular weight part a value of 34,000 is found, whereas the molecular weight of the other part has been determined to be 580,000 g mol^{-1}. Due to this large variation of the molecular weight, the polydispersity index, determined for fraction a, does not give a reliable value. The vinyl vibration is found at 1608 cm^{-1} (oligomer **4.28**: 1616 cm^{-1}). The ^{1}H-NMR spectrum of polymer **4.34** displays broad signals between 7 and 8 ppm for the aromatic and vinyl protons, and a broad signal at δ=2.7 ppm for the benzylic protons. Conductivity measure-

table 4.1 Physical characteristics of polymers **4.33** *and* **4.34**

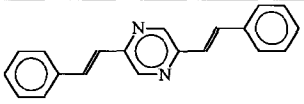
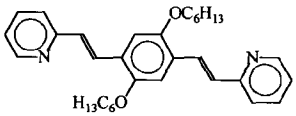
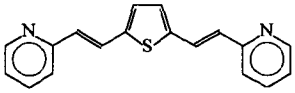
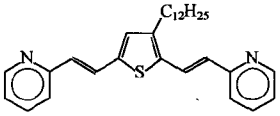
Polymer	Mw (g mol^{-1})	D	δ (S cm^{-1})
4.31	2.2 10^3	1.8	6.10^{-3}
4.32 a	3.4 10^4	3.3	2.10^{-3}
4.32 b	5.8 10^6		

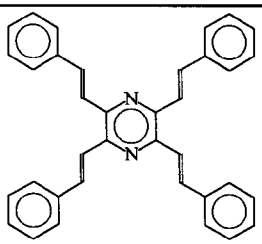
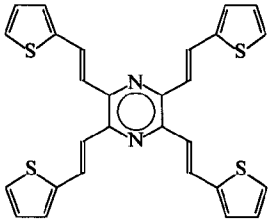
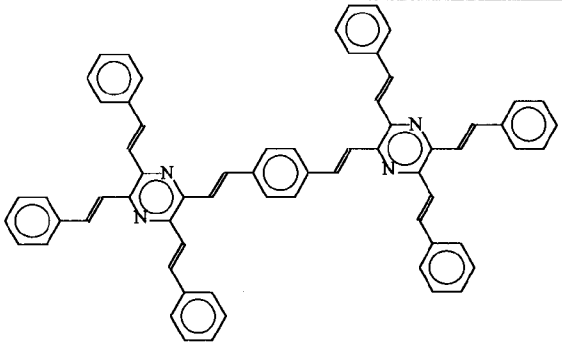
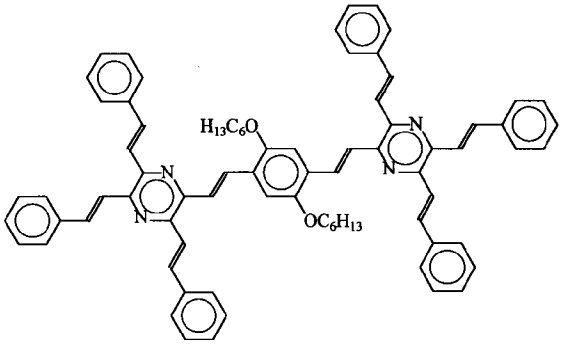
ments were performed on a thin film, cast from a chloroform solution by slow evaporation of the solvent, after oxidation with iodine. Although the molecular weights of polymers **4.33** and **4.34** are different, the conductivities have approximately the same values of 6. 10^{-3} and 2.10^{-3}, respectively. The data for the two polymers are summarized in table 4.1

4.4.1 Absorption spectroscopy

All the compounds are colored and (highly) fluorescent, displaying the planarity and through-conjugation. The absorption maxima are summarized in table 4.2 and 4.3. For the two-dimensional model compounds, the maximum absorption appears at approximately the same wavelength as seen in the one-dimensional compounds (for **4.27** the maximum is located at a shorter wavelength, but a shoulder of 90% relative intensity appears at 388 nm). However, a second maximum is found at a higher wavelength. This means that, although the number of linear through conjugated atoms is not increased, the effective conjugation length is enlarged indeed. For the oligomers there is a further red shift and the ε-values of this maximum are increased, although the shift of the absorption edge is only 30 nm for **4.30**. For polymer **4.33** on the other hand the maximum is shifted towards shorter wavelengths and also for the absorption edge there is no increase relative to oligomer **4.31**. For polymer **4.34**, there is a bathochromic shift, and especially the absorption edge is shifted considerably (approximately 160 nm compared with compound **4.28**).

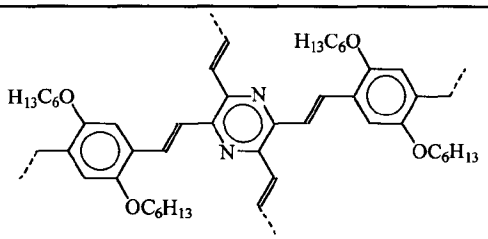
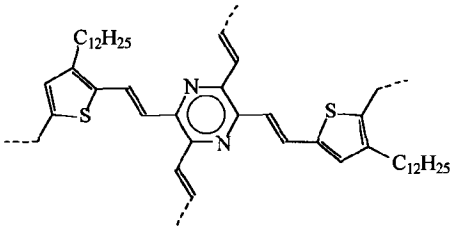
table 4.2 *UV data of selected model compounds and oligomers* (in $CHCl_3$)

compound	structure	λ_{max} (nm)
4.14		384.8
4.17		397.5
4.21		397
4.23		402

4.27		372 438 (0.51)[a]
4.28		400 419 (0.99)[a] 467 (0.55)[a]
4.30		465
4.31		475

a relative intensities

table 4.3 UV data of soluble polymers

compound	structure	λ_{max} (nm)
4.33		435 550[a]
4.34		466 700[a]

a absorption edge

4.4.2 X-ray analysis of compound 4.27

Ultimate proof of the conformation of the structures was obtained from X-ray analysis of compound **4.27**. X-ray quality crystals were obtained by crystallization from chloroform. The crystallographic results are summarized in figures 4.3 and 4.4 and tables 4.4 and 4.5. The compound crystallized in triclinic spacegroup $P\bar{1}$, Z=2, with unit cell dimensions a=9.520(1), b=9.637(1), c=14.243(1) Å. α = 90.93(1)° , β = 92.57(1)° , γ = 93.35(1)° , V = 1302.9(2) Å^3 . R_F=0.061. The data were collected from 3054 reflections. Figure 4.3 clearly displays the all-trans configuration of the molecule and the high degree of symmetry. The phenyl rings are in conjugation with the pyrazine ring, although the molecule is not entirely co-planar. Figure 4.4 demonstrates a twist of the phenyl rings of about 22 degrees relative to the pyrazine ring, but due to the connecting vinyl group, the loss of conjugation is very low. It is clear, however, from figure 4.3 that the distances between the protons, for example, H(3) and H(12) or H(2) and H(11)a are large enough to avoid sterical hindrance between the protons. This implies that the twist of the phenyl rings is a result of crystal packing, and not due to steric interactions.

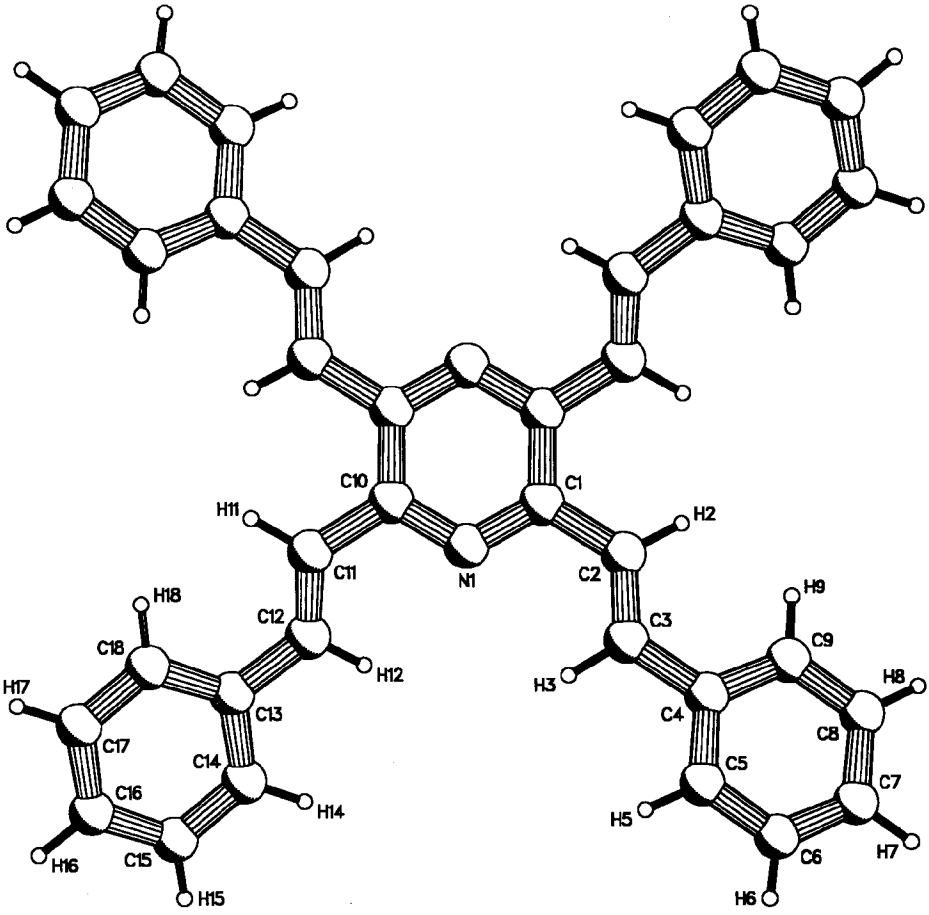


figure 4.3 PLUTO representation of **4.27**

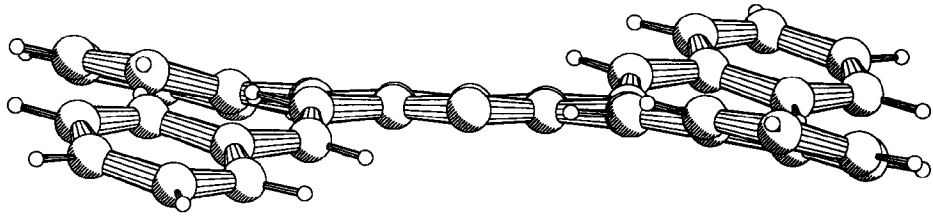


figure 4.4 PLUTO representation of **4.27** *viewed along the N-N axis*

table 4.4 *selected bond distances of* **4.27** (in Ångströms)

N(1)	-C(1)	1.334(5)	C(8)	-C(9)	1.381(6)
N(1)	-C(10)	1.334(4)	C(10)	-C(11)	1.468(5)
C(1)	-C(2)	1.469(6)	C(11)	-C(12)	1.334(6)
C(1)	-C(10)a	1.421(5)	C(12)	-C(13)	1.461(5)
C(2)	-C(3)	1.338(5)	C(13)	-C(14)	1.400(5)
C(3)	-C(4)	1.471(5)	C(13)	-C(18)	1.398(5)
C(4)	-C(5)	1.394(5)	C(14)	-C(15)	1.383(6)
C(4)	-C(9)	1.401(5)	C(15)	-C(16)	1.382(6)
C(5)	-C(6)	1.392(6)	C(16)	-C(17)	1.391(5)
C(6)	-C(7)	1.371(6)	C(17)	-C(18)	1.378(6)
C(7)	-C(8)	1.388(6)			

Numbers in parenthesis are estimated standard deviations in the last significant digits

table 4.5 *bond angles of* **4.27** (in degrees)

C(1)	-N(1)	-C(10)	118.9(3)	N(1)	-C(10)	-C(11)	116.6(3)
N(1)	-C(1)	-C(2)	117.8(3)	N(1)	-C(10)	-C(1)a	120.4(3)
N(1)	-C(1)	-C(10)a	120.7(3)	C(11)	-C(10)	-C(1)a	123.0(3)
C(2)	-C(1)	-C(10)a	121.6(4)	C(10)	-C(11)	-C(12)	122.2(4)
C(1)	-C(2)	-C(3)	123.7(4)	C(11)	-C(12)	-C(13)	127.2(4)
C(2)	-C(3)	-C(4)	125.2(4)	C(12)	-C(13)	-C(14)	118.1(3)
C(3)	-C(4)	-C(5)	119.8(3)	C(12)	-C(13)	-C(18)	123.9(3)
C(3)	-C(4)	-C(9)	122.2(3)	C(14)	-C(13)	-C(18)	118.0(3)
C(5)	-C(4)	-C(9)	117.9(3)	C(13)	-C(14)	-C(15)	120.8(4)
C(4)	-C(5)	-C(6)	120.6(4)	C(14)	-C(15)	-C(16)	120.7(4)
C(5)	-C(6)	-C(7)	120.6(4)	C(15)	-C(16)	-C(17)	118.8(4)
C(6)	-C(7)	-C(8)	119.7(4)	C(16)	-C(17)	-C(18)	120.9(4)
C(7)	-C(8)	-C(9)	120.1(4)	C(13)	-C(18)	-C(17)	120.7(4)
C(4)	-C(9)	-C(8)	121.1(4)				

Numbers in parenthesis are estimated standard deviations in the last significant digits

4.5 Discussion

The fact that the condensation of 2,3-dimethylquinoxaline and benzaldehyde only proceeds when crude benzaldehyde is used, shows that an acidic catalyst is required. The use of P_2O_5 has proven to be an excellent choice in the case of phenylene aldehydes, although the isolated yields of the compounds are somewhat low. This mainly stems from elaborated purifications since, especially in the case of **4.25** the reaction mixture consisted of several products.

When applied to thiophene aldehydes the P_2O_5 method could not be used due to the sensitivity of the thiophene compounds toward the catalyst, but good results were

obtained using benzoic anhydride. Again the purity of the catalyst should not be too high, since a small amount of acid is required for the reaction to proceed. The stability of the thiophene compounds is considerably lower than their phenyl analogues, and therefore, the synthesis of oligomers did not succeed. When 2,3,5-tris-(2-thiophen-2-yl-vinyl)-6-methylpyrazine was allowed to react with a dialdehyde a complex reaction mixture resulted, from which the oligomer could neither be isolated nor detected. The dodecyl substituted thiophene displays an enhanced reactivity compared with the unsubstituted material. This effect does not originate from electronic effects, since the alkyl substituent is electron donating and as a consequence the reactivity should decrease. Therefore, the explanation must be found in the solubilizing effect of the dodecyl substituent. For the dialdehydes this effect is not critical; dialdehyde **4.18** is very soluble, but for the mono-condensated products this solubility probably decreases considerably when the substituent is omitted. A strong argument in favor of this explanation is the fact that when the reaction of **4.18** is stopped after four days, the reaction mixture consist mainly of the mono-condensed product, which is not observed for **4.20**.

Side chains can be introduced readily and, as could be expected, have a positive effect on the solubility. Surprisingly, the introduction of the side chains has no negative effect on the conjugation length, not even in the case of compound **4.29**. Although the substituents cause an increase in the steric interactions, especially in the center of the molecule, there is no shift of the absorption maximum to shorter wavelengths. Symmetry is important for the solubility when side chains are introduced. Both compound **4.15** and **4.29**, which have two substituents, only show a moderate increase in solubility, whereas compound **4.21** is very soluble, as a result of one substituent minimizing the symmetry.

The compounds, containing phenylene as well as thiophene moieties, have a high degree of co-planarity and an all-trans double bond configuration (no cis double bonds have been detected). Although the phenyl rings in compound **4.25** are not entirely co-planar with the pyrazine ring, the distances between the protons of the different vinyl groups are large enough to conclude that this does not originate from steric interactions. Due to this conformation the compounds are highly conjugated. Important is that the two-dimensional compounds display an increase in effective conjugation length arising from their two-dimensionality. Thiophene containing compounds have absorption maxima higher than their phenylene analogues, presumably due to polarization of the molecule, since the pyrazine moieties are partly negative, and the thiophene rings partly positive.

Although polymer **4.30** is insoluble, preventing an accurate molecular weight determination by GPC, an estimation can be made. The molecular weight is well over 900,

since the molecular weight of oligomer **4.28**, which is slightly soluble, is 898. Furthermore oligomer **4.28** lacks any solubilizing substituents and has a higher degree of crystallinity. Polymer **4.30**, on the other hand, contains methyl and aldehyde functionalities, which are the unreacted end-groups. The molecular weight, however, is not likely to be much more than a few thousand, since the polymer precipitated from the reaction mixture, preventing any further growth, and the yield of 111% indicates the presence of substantial amounts of unreacted end-groups Polymer **4.31** has a low molecular weight and a λ_{max} at a shorter wavelength than oligomer **4.29**. It may not seem surprisingly therefore, that only a moderate conductivity is observed. However, polymer **4.32** has a considerably higher molecular weight and λ_{max} and especially the absorption edge indicates significant through-conjugation, but a conductivity comparable to that of **4.31**. Consequently, it is likely that these relative low conductivities also arise from a reduced charge carrier mobility because the nitrogen atoms act as a charge carrier sink, and are not completely due to an ineffective through-conjugation that results from the steric interactions of the solubilizing side chains.

4.6 Concluding remarks

In this chapter we have described the synthesis of pyrazine-containing model compounds, well-defined oligomers and polymers, via an improved acid catalyzed method. The introduction of two dimensional structures is accompanied by a considerable bathochromic shift of these compounds, compared with their one-dimensional analogues. Hence, the effective conjugation length increases for two-dimensional systems. Although the model compounds and oligomers prepared exhibit very attractive characteristics, the solubility problem immediately appears. The solubility can be increased by the introduction of side chains but then, a further increase in conjugation is only limited. Furthermore, the polymers only showed moderate conductivities, arising from both this small effective conjugation length and because of the nitrogen atoms acting as a charge carrier's sink.

4.7 Experimental section

For general remarks, see sections 2.7 and 3.5.

2,5-Dimethylpyrazine (**4.13**), 2-picoline (**4.15**), 2,3,5,6-tetramethylpyrazine (**4.24**) and terephthaldehyde (**4.29**) were purchased from Janssen Chimica. 2,3-Dimethylquinoxaline was synthesized according to reference 22. The synthesis of compounds **4.16**, **4.20** and **4.22** is described in chapter three.

X-ray data collection was performed by Mr. A. Meetsma with Mo Kα radiation on an Enraf-Nonius CAD-4F diffractometer interfaced to a VAX-11/730 computer.

2,3-Distyrylquinoxaline (4.12)

A mixture of 2,3-dimethylquinoxaline (**4.11**) (1 g, 6.3 mmol) and crude benzaldehyde (**4.4**) (10 ml) was refluxed for 3.5 h. After cooling the resulting dark mixture was poured into pentane. The solid was collected and recrystallized from EtOH. This afforded 1.15 g (54%) of **4.12** as yellow crystals. mp: 195.9-196.8°C. ^{1}H-NMR ($CDCl_3$) δ:7.42 (m, 6H), 7.65 (m, 8H), 8.01 (d, J=15.8 Hz, 2H), 8.05 (m, 2H) ppm. ^{13}C-NMR ($CDCl_3$) δ:122.5 (d), 127.5 (d), 128.7 (d), 128.9 (d), 129.3 (d), 136.3 (s), 137.7 (d), 141.4 (s), 148.9 (s) ppm.

2,5-Distyrylpyrazine (4.14)

A solution of 2,5-dimethylpyrazine (**4.13**) (1.2 g, 11 mmol) in crude benzaldehyde (**4.4**) (10 ml) was refluxed for two days. The colored mixture was poured in 50 ml EtOH, the resulting solid collected and recrystallized from toluene. This afforded 1.55 g (50%) of **4.14** as yellow crystals. mp: 218.5-219.7 °C (lit[5] 219-220 °C). UV:($CHCl_3$) λ_{max} 384.8 nm. ^{1}H-NMR ($CDCl_3$) δ: 7.19 (d, J=16.2 Hz, 2H), 7.39 (m, 6H), 7.61 (m, 4H), 7.75 (d, J=16.2 Hz, 2H), 8.60 (s, 2H) ppm.

2,5-Bis-hexyloxy-1,4-bis-(2-pyridin-2-yl-vinyl) benzene (4.17)

A mixture of 2,5-dihexyloxy terephthaldehyde (**4.16**) (1 g 3 mmol), 2-picoline (**4.15**) (700 mg, 7.5 mmol) and P_2O_5 (300 mg, 2.1 mmol) in DMF (45 ml) and o-xylene (5 ml) was refluxed for 20 h. After cooling the dark colored mixture was poured in water (150 ml) and extracted with CH_2Cl_2 (4x50 ml). The combined organic layers were washed with water, a $NaHCO_3$ solution, water, brine and dried over $MgSO_4$. After removal of the solvent the residue was chromatographed over silicagel. CH_2Cl_2 was used as eluent first to remove impurities and was then changed into a mixture of CH_2Cl_2 and EtOAc (1:1) to give **4.17**. Recrystallization from i-PrOH afforded 500 mg (35%) of **4.17** as a bright yellow solid mp: 99.5-100.3°C. UV:($CHCl_3$) λ_{max} 397.5 nm. ^{1}H-NMR ($CDCl_3$) δ:0.95 (t, 6H), 1.40 (m, 8H), 1.55 (m, 4H), 1.90 (m, 4H), 4.10 (t, 4H), 7.15 (m, 2H), 7.22 (s, 2H), 7.33 (d, J=16.8 Hz, 2H), 7.51 (d, 2H), 7.67 (m, 2H), 7.91 (d, J=16.8 Hz, 2H), 8.64 (d, 2H) ppm. ^{13}C-NMR ($CDCl_3$) δ:13.9 (q), 22.5 (t), 25.8 (t), 29.3 (t), 31.5 (t) 69.2 (t), 111.2 (d), 121.2 (d), 121.6 (d), 126.5 (s), 127.5 (d), 128,9 (d), 136.2 (d) 149.4 (d), 151.2 (s), 156.2 (s) ppm. Anal. calc. for $C_{32}H_{40}N_2O_2$: C 79.30, H 8.32, N 5.78, found: C 78.99, H 8.48, N 5.78. HRMS calc. for $C_{32}H_{40}N_2O_2$: 484.309; found: 484.309.

2,3-Bis-(2-thiophen-2-yl-vinyl) quinoxaline (4.19)

A mixture of thiophene-2-carbaldehyde (**4.18**) (2.1 g, 18.7 mmol), 2,3-dimethyl quinoxaline (**4.11**) (1.48 g, 9.3 mmol) and benzoic anhydride (4.3 g) in o-$C_6H_4Cl_2$ (35 ml) was refluxed for 8 h. The solvent was removed and the residue stirred in 1N KOH overnight and extracted with CH_2Cl_2 (3x100 ml). The combined organic layers were washed with water, brine and dried (Na_2SO_4). The solvent was evaporated and the residue chromatographed (silica, CH_2Cl_2). Crystallization from EtoH afforded 700 mg (22%) of **4.19** as yellow crystals. mp:206.7-207.6°C. ^{1}H-NMR ($CDCl_3$) δ:7.08 (dd, 2H), 7.33 (m, 4H), 7.39 (d, J=15.4 Hz,

2H), 7.55 (m, 2H), 7.99 (m, 2H), 8.13 (d, J=15.4 Hz, 2H).^{13}C-NMR ($CDCl_3$) δ:121.4 (d), 126.4 (d), 127.9 (d), 128.6 (d), 128.9 (d), 129.3 (d), 130.3 (d), 141.4 (s), 141.9 (s), 148.3 (s). Furthermore was obtained 790 mg of **2-(2-thiophen-2-yl-vinyl)-3-methyl quinoxaline**. mp:100.1-102°C. ^{1}H-NMR ($CDCl_3$) δ:2.86 (s, 3H), 7.07 (dd, 1H), 7.28 (m, 3H), 7.66 (m, 2H), 7.99 (m, 2H), 8.18 (d, J=15.0 Hz, 1H).

2,5-Bis-(2-pyridin-2-yl-vinyl) thiophene (4.21)

A solution of thiophene-2,5-dicarbaldehyde (**4.20**) (400 mg, 2.86 mmol), 2-picoline (**4.15**) (1 ml) and benzoic anhydride (2 g) in o-$C_6H_4Cl_2$ (10 ml) was refluxed for 9 days. The solvent and excess 2-picoline were removed and to the residue a NaOH solution was added. This mixture was stirred overnight, extracted with CH_2Cl_2 (3x75 ml) and the organic layers were washed with water, brine and dried (Na_2SO_4). Evaporation of the solvent and column chromatography (Al_2O_3, CH_2Cl_2) afforded 50 mg (6%) of **4.21** as a yellow solid. mp: 133.5-134.4°C. UV:($CHCl_3$) λ_{max} 397 nm. ^{1}H-NMR ($CDCl_3$) δ:6.96 (d, J=15.4 Hz, 2H), 7.13 (ddd, J=7.7 Hz, J=4.7 Hz, J=1.3 Hz, 2H), 7.32 (d, J=7.7 Hz, 2H), 7.65 (dt, J=7.7 Hz, J=1.7 Hz, 2H), 7.75 (d, J=15.8 Hz, 2H), 8.59 (d, J=3.85 Hz, 2H) ppm. HRMS calc. for $C_{18}H_{14}N_2S$: 290.088; found 290.088.

3-Dodecyl-2,5-bis-(2-pyridin-2-yl-vinyl) thiophene (4.23)

A mixture of 3-dodecylthiophene-2,5-dicarbaldehyde (**4.22**) (1 g, 3.25 mmol), 2-picoline (**4.15**) (0.9 g, 10 mmol) and benzoic anhydride (2.2 g) in o-$C_6H_4Cl_2$ (30 ml) was refluxed for 72 h. The solvent was evaporated, H_2O, NaOH and EtOH were added to the residue and this mixture was stirred for 4 h. After the EtOH was evaporated, the aqueous phase was extracted with CH_2Cl_2 (3x100 ml). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and the solvent evaporated. The residue was chromatographed (silica, CH_2Cl_2, 5% EtOAc) and recrystallized from hexane giving 450 mg (30%) of **4.23** as yellow crystals. mp: 91.9-94.3°C UV:($CHCl_3$) λ_{max} 402 nm. ^{1}H-NMR ($CDCl_3$) δ:0.85 (t, 3H), 1.23 (m, 18H), 1.59 (m, 2H), 2.67 (t, 2H), 6.89 (d, J=15.6 Hz, 1H), 6.91 (d, J=15.7 Hz, 1H), 6.92 (s, 1H), 7.06 (m, 2H), 7.24 (d, J=7.3 Hz, 2H), 7.58 (dt, J=7.6 Hz, J=1.7 Hz, 2H), 7.68 (d, J=15.7 Hz, 1H), 7.80 (d, J=15.5 Hz, 1H), 8.55 (m, 2H) ppm. ^{13}C-NMR ($CDCl_3$) δ:13.9 (q), 22.5 (t), 26.2 (t), 29.2 (t), 29.3 (t), 29.5 (t), 30.6 (t), 31.7 (t), 121.5 (d), 121.7 (d), 122.0 (d), 122.1 (d), 123.5 (d), 125.4 (d), 126.9 (d), 127.4 (d), 130.7 (d), 136.0 (s), 136.2 (d), 140.1 (s), 143.7 (s), 149.5 (d), 154.9 (s), 155.1 (s) ppm. anal. calcd. for $C_{28}H_{38}N_2S$: C 78.55, H 8.35, N 6.11, S 6.99, found: C 78.31, H 8.39, N 6.18, S 7.09. HRMS calcd. for $C_{28}H_{38}N_2S$: 458.276, found: 458.276.

2,3,5,6-Tetrastyrylpyrazine (4.27)

A mixture of 2,3,5,6-tetramethylpyrazine (**4.24**) (2.0 g, 15 mmol), freshly distilled benzaldehyde (**4.4**) (7.4 g, 70 mmol), P_2O_5 (4 g), DMF (90 ml) and xylene (10 ml) was refluxed under a nitrogen atmosphere for 6 days. The resulting dark fluorescent mixture was cooled and poured into water (250 ml), the organic layer separated and the water layer extracted with CH_2Cl_2 (4x75 ml). The combined organic layers were washed with water, a $NaHCO_3$ solution, brine and dried over $MgSO_4$. Evaporation of the solvents afforded a dark colored oil, that was distilled (kugelrohr, 80°C 0.1 mbar) to remove the last traces of DMF and benzaldehyde. The residue was filtered (silicagel, CH_2Cl_2) to give 4.3 g of a mixture of **4.25**, **4.26** and **4.27**. This was dissolved in $CHCl_3$ and chromatographed (silicagel CH_2Cl_2-pentane 1:1), to give: 920 mg (12%) of **4.27**

as orange needles (recrystallized from toluene) mp: 248.1-250.7 °C. UV: ($CHCl_3$) λ_{max} 371 nm ε=54.870; λ_{max}, 438 nm ε=27.824. ^{1}H-NMR ($CDCl_3$) δ:7.40 (m, 12H), 7.52 (d, J=16,2 Hz, 4H), 7.66 (d, 8H), 7.96 (d, J=16,2 Hz, 4H) ppm. ^{13}C-NMR ($CDCl_3$) δ:122.09 (d), 127.34 (d), 128.53(d), 128.65(d), 135.67 (d), 136.71 (s), 145.03 (s) ppm. IR (KBr) cm^{-1}: 3078 (w), 3055 (w), 3020 (w), 1624 (m), 1493 (m), 1450 (m), 1384 (m), 1165 (s), 960 (s), 744 (s), 686 (s). Anal. calcd. for $C_{36}H_{28}N_2$: C 88.49, H 5.78, N 5.73, found: C 88.97, H 5.89, N 5.76. HRMS calc. for $C_{36}H_{28}N_2$: 488.225; found: 488.225. 230 mg (4%) of **2,3,5-tristyryl-6-methylpyrazine** (**4.26**) as a dark yellow solid (recrystallized from CH_2Cl_2 / i-PrOH) mp: 178.0-180.3 °C. ^{1}H-NMR ($CDCl_3$): δ 2.68 (s, 3H); 7.29 (d, J=16.1 Hz, 1H), 7.41 (m, 11H), 7.63 (m, 6H), 7.84 (d, J=16.1 Hz, 1H), 7.91 (d, J=15.4 Hz, 1H), 7.94 (d, J=15,4 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$) δ:21.6 (q), 122.0 (d), 122.1 (d), 122.5 (d), 127.2 (d), 128.3 (d), 128.4 (d), 128.5 (d), 134.9 (d), 135.0 (d) 136.6 (s), 136.7 (s), 144.3 (s), 144.5 (s), 146.1 (s), 149.0 (s) ppm. HRMS calcd. for $C_{29}H_{24}N_2$: 400.194; found: 400.194. And 630 mg. (13%) of **2,5-distyryl-3,6-dimethylpyrazine** (**4.25c**) as a yellow solid (recrystallized from $CHCl_3$) mp: 217.6-218.5 °C. ^{1}H-NMR ($CDCl_3$) δ:2.68 (s, 6H), 7.27 (d, J=15.4 Hz, 2H), 7.34 (m, 6H), 7.59 (d, 4H), 7.81 (d, J=15.4 Hz, 2H) ppm. ^{13}C-NMR ($CDCl_3$) δ:21.36 (q), 122.69 (d), 127.15 (d), 128.34 (d), 128.58 (d), 134.38 (d), 136.73 (s), 145.92 (s), 147.96 (s) ppm. IR (KBr) cm^{-1}: 3078 (w), 3055 (w), 3020 (w), 2957 (w), 2921 (w), 1628 (m), 1489 (m), 1447 (m), 1393 (m), 1211 (m), 1138 (m), 964 (s), 748 (s), 694 (s). HRMS calcd. for $C_{22}H_{20}N_2$: 312.162; found: 312.163.

2,3,5,6-Tetrakis-(2-thiophen-2-yl-vinyl) pyrazine (4.28)

A mixture of thiophene-2-carbaldehyde (**4.18**) (5.65 g, 50 mmol), 2,3,5,6-tetramethylpyrazine (**4.24**) (1.17 g, 8.6 mmol) and benzoic anhydride (7.8 g) in o-$C_6H_4Cl_2$ (60 ml) was refluxed for 5 days. The solvent was evaporated and to the residue H_2O and NaOH were added and this mixture was stirred overnight. It was extracted with CH_2Cl_2 (3x250 ml) and the combined organic layers were washed with water, brine and dried (Na_2SO_4). The solvent was evaporated and the mixture chromatographed (silica, CH_2Cl_2-pentane 1:1) affording 120 mg (3%) of **4.28** as a dark red solid (recrystallized from $CHCl_3$). mp: 230°C (d). UV:($CHCl_3$) λ_{max} 400, 419, 467 nm.(relative intensities of 1, 0.99 and 0.55 respectively) ^{1}H-NMR ($CDCl_3$) δ:7.09 (m, 4H), 7.29 (m, 12H), 8.06 (d, J=15.4 Hz, 4H) ppm. ^{13}C-NMR ($CDCl_3$) δ:121.2 (d), 125.9 (d), 127.9 (d), 128.2 (d), 128.4 (d), 142.3 (s), 144.5 (s) ppm. IR (KBr) cm^{-1}: 3063 (w), 1616 (s), 1389 (m), 1323 (m), 1218 (m), 1200 (m), 1161 (m), 953 (s), 856 (m), 814 (m), 690 (s). Anal. calcd. for $C_{28}H_{20}N_2S_4$: C 65.59, H 3.93, N 5.46, S 25.01, found: C 65.47, H 3.87, N 5.58, S 24.54. HRMS calcd. for $C_{28}H_{20}N_2S_4$: 512.051; found: 512.051. Further were isolated 360 mg (10%) of **2,3,5-tris-(2-thiophen-2-yl-vinyl)-6-methylpyrazine** as a bright orange solid with strong fluorescence mp: 185.6-187.0°C. ^{1}H-NMR ($CDCl_3$) δ:2.69 (s, 3H), 7.08 (m, 3H), 7.27 (m, 9H), 7.96 (d, J=15.0 Hz, 1H), 8.03 (d, J=15.4 Hz, 1H), 8.05 (d, J=15.4 Hz, 1H) ppm. HRMS calc. for $C_{23}H_{18}N_2S_3$: 418.063; found 418.063. And 340 mg (12%) of **2,5-di-(2-thiophen-2-yl-vinyl)-3,6-dimethylpyrazine** as an orange solid (recrystallized from EtOH) mp:179.8-181.2°C.^{1}H-NMR ($CDCl_3$) δ:2.64 (s, 6H), 7.04 (m, 2H), 7.07 (d, J=15.3 Hz, 2H), 7.21 (d, 2H), 7.27 (d, 2H), 7.94 (d, J=15.0 Hz, 2H) ppm. ^{13}C-NMR ($CDCl_3$) δ:21.3 (q), 122.0 (d), 125.5 (d), 127.1 (d), 127.7 (d), 128.0 (d), 142.4 (s), 145.4 (s), 147.8 (s) ppm. IR (KBr) cm^{-1}: 3098 (w), 2920 (w), 1616 (s), 1420 (m), 1393 (s), 1342 (m), 1211 (s), 1122 (m), 957 (s), 852 (m), 825 (m), 698 (s). HRMS calc. for $C_{18}H_{16}N_2S_2$: 324.075; found 324.075.

1,4-Bis-[2-(3,5,6-tristyryl-pyrazin-2-yl)-vinyl]-benzene (4.30)

A mixture of 2,3,5-tristyryl-6-methylpyrazine (**4.26**) (200 mg, 0.5 mmol), terephthaldehyde (**4.29**) (33.5 mg, 0.25 mmol) P_2O_5 (50 mg) in DMF (20 ml) and xylene (2 ml) was refluxed for two days. The dark mixture was poured in water and the solid collected. The solid was washed water, EtOH and $CHCl_3$ to afford 100 mg (44%) of **4.30** as a red solid. mp: >250°C. UV $\lambda_{max}(CHCl_3)$: 465 nm. IR (KBr) cm^{-1}: 3055 (w), 1627 (m), 1493 (m), 1385 (m), 1169 (s), 964 (s), 744 (s), 687 (s).

2,5-Bis-hexyloxy-1,4-bis-[2-(3,5,6-tristyryl-pyrazin-2-yl)-vinyl]-benzene (4.31)

A mixture of 2,3,5-tristyryl-6-methylpyrazine (**4.26**) (100 mg, 0.25 mmol), 2,5-dihexyloxy terephthaldehyde (**4.16**) (41 mg, 0.125 mmol) and P_2O_5 (20 mg) in DMF (10 ml) and xylene (1 ml) was refluxed for 4 days. The mixture was poured in water and the resulting solid collected. Crystallization from $CHCl_3$ afforded 20 mg (15%) of **4.31** as a dark red solid. mp: 290°C (d). UV:($CHCl_3$) λ_{max} 475 nm. ^{1}H-NMR ($CDCl_3$) δ:0.91 (t, 6H), 1.45 (m, 12H), 1.95 (m, 4H), 4.14 (t, 4H), 7.35 (m, 6H), 7,44 (m, 12H), 7.58 (d, J=15.1 Hz, 4H), 7.60 (d, J=15.6, 2H), 7.70 (m, 12H), 7.81 (d, J=15.6, 2H), 7.99 (d, J=15.6, 2H), 8.00 (d, J=15.6, 2H), 8.02 (d, J=15.6, 2H), 8.24 (d, J=15.6, 2H) ppm.

Poly-(pyrazine-2,3,5,6-tetrayl)-2-(phenylen-1,4-diyl)vinylene (4.32)

A mixture of 2,3,5,6-tetramethylpyrazine (**4.24**) (1.0020 g, 7.357 mmol), terephthaldehyde (**4.29**) (1.9737 g, 14.714 mmol), P_2O_5 (2 g), xylene (7 ml) and DMF (70 ml) were refluxed for 6 days. The suspension was poured in water, the solid collected and washed successively with water, EtOH, CH_2Cl_2 and o-$C_6H_4Cl_2$ affording 2.7 g of **4.32** as an insoluble dark red solid. IR (KBr) cm^{-1}: 3437 (b), 1663 (s), 1624 (s), 1508 (w), 1385 (m), 1130 (m), 964 (s), 810 (m).

Poly-(pyrazine-2,3,5,6-tetrayl)-2-(1,4-dihexyloxyphenylen-1,4-diyl)vinylene (4.33)

A mixture of 2,5-dihexyloxy terephthaldehyde (**4.16**) (488.7 mg, 1.461 mmol), 2,3,5,6-tetramethylpyrazine (**4.24**) (99.5 mg, 0.7305 mmol), P_2O_5 (200 mg), xylene (5 ml) and DMF (50 ml) was refluxed for 4 days. The dark reaction mixture was poured in water and the aqueous phase extracted with CH_2Cl_2 (4x50 ml). The combined organic layers were washed with water, a $NaHCO_3$ solution and dried ($MgSO_4$). The solvents were evaporated and the solid residue dissolved in 5 ml CH_2Cl_2 and precipitated in hexane to afford 370 mg (69%) of **4.33** as a red solid. UV:($CHCl_3$) λ_{max} 435 nm. (absorption edge at approximately 550 nm) IR (KBr) cm^{-1}: 2932 (s), 2858 (m), 1674 (m), 1616 (w), 1504 (m), 1207 (s), 1022 (m).

Poly-(pyrazine-2,3,5,6-tetrayl)-2-(3-dodecylthiophen-2,5-diyl)vinylene (4.34)

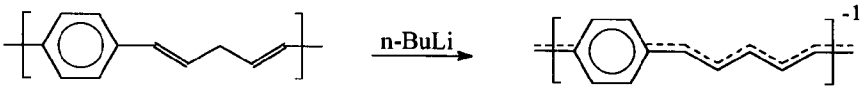
A solution of 3-dodecyl-thiophene-2,5-dicarbaldehyde (**4.22**) (3.0002 g, 9.726 mmol), 2,3,5,6-tetramethylpyrazine (**4.24**) (677.0 mg, 4.863 mmol) and benzoic anhydride (9 g) in dichlorobenzene (50 ml) was refluxed for 5 days. The dark red mixture was cooled, poured in EtOH and the resulting solid collected. Further purification was carried out by stirring the solid overnight in EtOH. Filtration and drying afforded 2.82 g (85%) of **4.34**. UV:($CHCl_3$) λ_{max} 466 nm. (absorption edge at approximately 700 nm) IR (KBr) cm^{-1}: 2924 (s), 2851 (s), 1662 (s), 1608 (s), 1454 (m), 1211 (m), 1126 (m), 953 (m).

Chapter five

Toward a stable n-doped conducting polymer

5.1 Introduction

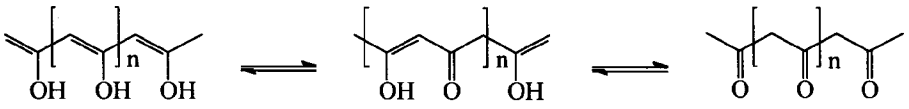
Virtually all conjugated polymers are insulators in the neutral state. To obtain conductivity, charge carriers must be generated, either positively or negatively charged, resulting in p-doped and n-doped materials, respectively. p-Doping is achieved by oxidation of the materials, either during synthesis (electrochemically or oxidatively) or by the addition of an oxidant to the virgin polymer. Reduction affords n-doped polymers, but this is far more difficult to achieve and the materials are less stable than their oxidized counterparts. Consequently, p-doped conducting polymers have attracted most attention. Reduction with Na_2S (instead of Na or K) has been found to be effective when applied to polymers with a positively charged nitrogen atom in the polymer chain, resulting in a n-type self-doped conducting polymer[1]. Alternatively, charge carriers can be generated by protonation or deprotonation of suitable precursor polymers. The concept of protonation has been applied successfully to polyaniline, where the so-called 'protonic acid doping' yields a stable, highly conducting p-doped polymer[2]. Similarly, proton abstraction has been used for the introduction of charge carriers, affording a n-type polymer. An initial attempt at the synthesis of n-doped polyacetylene by deprotonation was carried out on a copolymer of acetylene and 1,3-butadiene, but it was impossible to achieve exhaustive deprotonation[3]. Better results have been obtained by the deprotonation of segmented polyacetylene[4], a polymer generated by quenching n-doped polyacetylene with methanol. Another example is depicted in scheme 5.1[5]. Deprotonation of poly(p-phenylene pentadienylene) with n-butyllithium yields a blue-black polymer with a conductivity up to 1 S cm^{-1}. Although conductive, the polymer is not stable under ambient conditions, due to the high reactivity of the generated anion.



scheme 5.1

1 Zhang, N.; Wu, R.; Li, Q.; Pakbaz, K.; Yoon, C. O.; Wudl, F. *Chem. Mater.* **1993**, *5*, 1598
2 Chiang, J.-C.; MacDiarmid, A. G. *Synth. Met.* **1986**, *13*, 193
3 Tolbert, L. M.; Schomaker, J. A.; Holler, F. J. *Synth. Met.* **1986**, *15*, 195
4 Tolbert, L. M.; Schomaker, J. A. *Synth. Met.* **1991**, *41-43*, 165
5 Gordon III, B.; Hancock, L. F. *Polymer* **1987**, *28*, 585

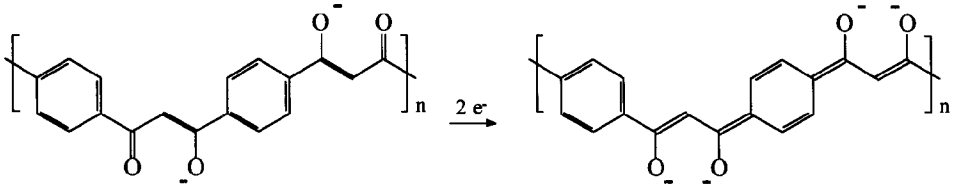
Improving the stability of these poly-anions would provide materials with attractive properties. The stability can be increased by coordination of the anion to a metal cation. Effective coordination, however, is only achieved if the anion contains heteroatoms, improving its chelating properties. A good ligand is the 1,3-diketone moiety, which after deprotonation forms stable complexes with various metal cations, the negative charge is delocalized over the two oxygen atoms and the methylene group. The 1,3-diketone moiety has been subject of some research; poly(ketene) (PKT, figure 5.1) has been prepared and studied[6]. The conjugation in PKT, however, is limited due to the relative instability of the



a

figure 5.1

all-enol isomer (figure 5.1 a)[7]. Calculations have suggested that a polymer with 1,3-diketone functionalities connected by double bonds are conjugated and have a band gap of 1.2eV, allowing it to become conducting upon doping[7]. Therefore, we have designed a synthesis of a poly-1,3-diketone with the diketone functionalities connected by phenyl rings. Upon deprotonation and complexation this is expected to result in a polyanion as depicted in figure 5.2 a. Furthermore, the generated polyanion can be reduced, resulting in a partly quinoid structure (figure 5.2 b), which can be regarded as the n-type analog of



a b

figure 5.2

polyaniline. 1,3-Diketones have been synthesized by the condensation of acetyl compounds with esters or acid chlorides, using a strong base, usually sodium amide[8]. The

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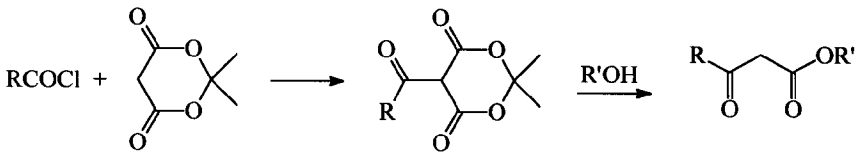
6 a) Olah, G. A.; Zadok, E.; Edler, R.; Adamson, D. H.; Kasha, W.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1989**, *111*, 9123 b) Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1989**, *111*, 9124

7 Cui, C. X.; Kertesz, M. *J. Am. Chem. Soc.* **1991**, *113*, 4404

8 a) Adams, J. T.; Hauser, C. R. *J. Am. Chem. Soc.* **1944**, *66*, 1220 b) Linn, B. O.; Hauser, C. R. *J. Am. Chem. Soc.* **1956**, *78*, 6066

yields in these syntheses are, however, only satisfactory when an excess of ketone is used. With equimolar amounts of reactants only moderate yields are obtained, making these methods unsuitable for the synthesis of 1,3-diketone polymers. Higher yields can be obtained when the protons of the ketone moiety are activated, i.e., made more acidic. This can be accomplished by the introduction of a second carbonyl functionality, e.g., an ester group. When 1,3-keto esters are condensed with esters or acid chlorides, the reaction proceeds in high yields, but a competition of C- and O-acylation can occur. The ratio of O- vs. C-acylation is dependent on the base used, and therefore can be shifted in either direction[9]. Triethyl amine affords a mixture of both C- and O-acylated products in a ratio of 0.6, whereas with pyridine the ratio is 0.03. On the other hand, dimethyl aniline gives complete C-acylation. Besides the high yields, important for the preparation of polymers, the route offers an extra advantage. Introduction of the ester functionality involves substitution of the rigid backbone, and the use of longer esters will result in the formation of soluble compounds. For the synthesis of β-keto esters several methods are available, using various condensations[10]. A promising method is the use of Meldrum's acid (**5.1**), in which an acid chloride can be converted into the β-keto ester with any ester required[11]



5.1

scheme 5.2

(scheme 5.2). Alternatively, high yields of β-keto esters are obtained upon the reaction of acid chlorides with dilithio monoethyl malonate (**5.2**, scheme 5.3). High yields are convenient, especially when bifunctional compounds are prepared (monomers).

Complexation of 1,3-diketone moieties is well documented. Especially 1,3-diphenylpropane-1,3-dione (dibenzoylmethane) has been examined and several complexes have been described with metal ions such as copper, nickel and iron, simply by mixing the

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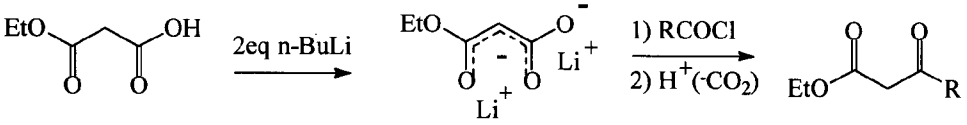
9 Wright, P. E.; McEwen, W. E. *J. Am. Chem. Soc.* **1954**, *76*, 4540

10 For an enumeration of the large number of available methods, see reference 5 in: Wierenga, W.; Skulnick, H. I. *Org. Synth.* **1983**, 61, 5

11 a) Oikawa, Y.; Sugano, K.; Yonemitsu, O., *J. Org. Chem.* **1978**, *43*, 2087 b) Hase, T. A.; Salonen, K. *Synth. Commun.* **1980**, *10*, 221



5.2

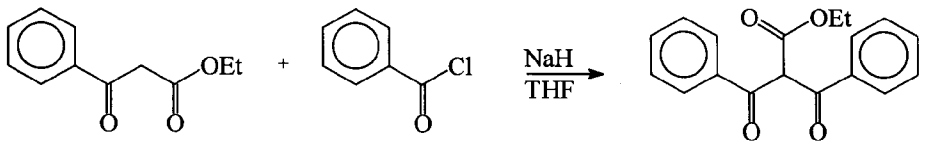
scheme 5.3

ketone and the metal salt together with a base[12]. With the introduction of an ester functionality, the examples of complexation are less frequent, but for the methyl ester of 2-benzoyl-3-oxo-3-phenyl-propionic acid the copper complex has been prepared similarly. The complexes with copper have a dimeric structure and consist of two ketone moieties attached perpendicular to each other to copper. When applied to polymers, this results in the cross-linking of the polymer chains, accompanied by a decrease in solubility, and possibly followed by the precipitation of the polymer from the reaction mixture. Due to this precipitation, the deprotonation of the ketone functionalities will be incomplete. Consequently, both the concentration and the mobility of the generated charge carriers in the material will be too low for attractive electrical properties. The use of longer esters might be helpful, but only to a minor extent. Alternatively, this cross-linking can be prevented by the synthesis of mixed complexes with at one side of the metal ion the polymer chain, and at the other side another ligand such as acetylacetone.

In this chapter we will describe the synthesis of model compounds and polymers containing the 1,3-diketone moiety, and study the complexation of these materials with copper ions. For the deprotonation both the complexation of polymer chains only, and the mixed complex strategies are examined.

5.2 Synthesis of 1,3-diketones

The condensation of acetyl compounds with acid chlorides provided the 1,3-diketones in moderate yields, making this approach unsuitable for the preparation of

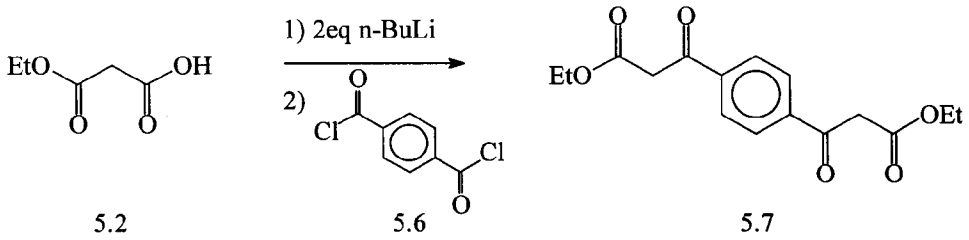


5.3 5.4 5.5

scheme 5.4

12 Beilstein's "*Handbuch der Organischen Chemie*" 7, III, 3838

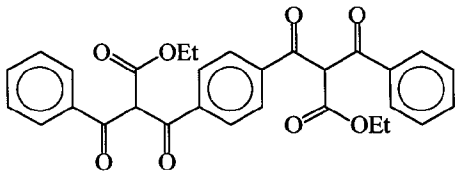
polymers. Therefore, we turned to the synthesis of 1,3-diketones with ester functionalities in the 2-position, readily synthesized from β-keto acids and acid chlorides. Although the use of dimethyl aniline afforded the products in high yields, the relatively low reactivity (reaction times as long as 24 hours were required for complete conversion), prompted us to use a different base. It turned out that sodium hydride met the requirements, namely complete C-acylation and high conversions. Thus, ethyl benzoylacetate (**5.3**) was deprotonated with sodium hydride and the anion quenched with benzoylchloride (**5.4**), to afford ethyl 2-benzoyl-3-oxo-3-phenyl-propionate (**5.5**) in 81% yield (scheme 5.4). The characterization of **5.5** is not trivial due to the existence of keto-enol isomers. In the ^{1}H-NMR, the all-keto and two different enol isomers are found, the ratio depends on the solvent. Demonstration of the complete C-acylation on the other hand is straightforward. Treatment of the reaction mixture with a cold KOH solution affords the water soluble anion, whereas the O-acylated product does not dissolve. Analysis of the corresponding organic phase clearly established the absence of the O-acylated product. For the synthesis of a polymer we turned to the AA-BB-polymerization. The bis-β-keto ester **5.7** was synthesized as outlined in scheme 5.5. Terephthaloyl chloride and two equivalents of the



5.2 5.6 5.7

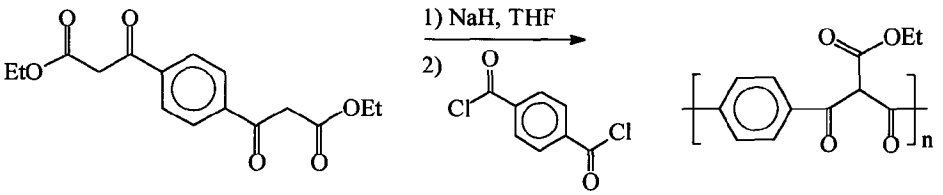
scheme 5.5

bis-lithium derivative of monoethyl malonate (**5.2**) were allowed to react, to afford **5.7** in 48% yield. In solution, the compound consists of three isomers; the all-keto, the all-enol and the keto-enol isomer. The different isomers are easily recognized in the ^{1}H-NMR spectrum in which the aromatic region displays two singlets and an AB-pattern. We used



5.8

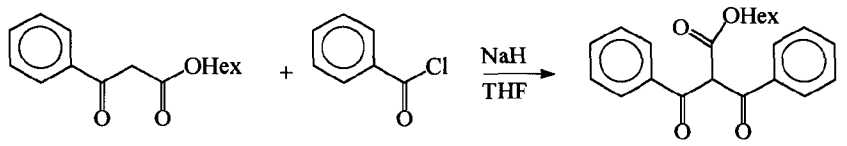
this method although the introduction of other ester groups requires extra reactions, because the alternative method using Meldrum's acid (**5.1**) failed for aromatic acid chlorides. This method would provide an easy way for the introduction of other esters (R') simply by the reaction of the intermediate product with the appropriate alcohol (see scheme 5.2). Both the condensation of **5.7** with benzoyl chloride (**5.4**) and the reaction of ethyl benzoylacetate (**5.3**) and terephthaloyl chloride (**5.6**) afforded compound **5.8** in yields of 75 to 80%. Proof of the structure for **5.8** is complicated by the existence of several keto-enol isomers. However, IR spectroscopy and the solubility of **5.8** in a KOH solution strongly suggest that **5.8** has the assigned structure. From the high conversions in the reactions of **5.6** and **5.7**, it can be deduced that both compounds are suitable monomers for the synthesis of a polymer. Polymerization of monomers **5.6** and **5.7** was carried out under identical conditions, giving **5.9** in a yield of 90% (scheme 5.6). However, the polymer was



5.7 5.6 5.9

scheme 5.6

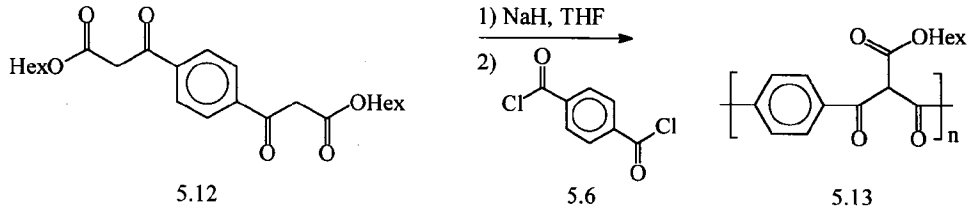
only partly soluble in, for example, THF and chloroform. To improve the solubility, the hexyl ester was used, which was readily introduced by trans-esterification of both **5.3** and **5.7** with hexanol, affording **5.10** and **5.12**, respectively. The condensation of **5.10** with benzoyl chloride (**5.4**) afforded the hexyl-substituted model compound **5.11** as a very soluble white solid in 65% yield (scheme 5.7). Similarly, terephthaloyl chloride (**5.6**) and



5.10 5.4 5.11

scheme 5.7

monomer **5.12** afforded polymer **5.13** in a yield of 80% (scheme 5.8). The polymer was of high purity and displayed the expected solubility in organic solvents such as chloroform and THF. GPC analysis relative to polystyrene standards revealed the presence of some low molecular weight material, and the molecular weight was estimated at M_n=2360 g mol^{-1} with D=8.



5.12 5.6 5.13

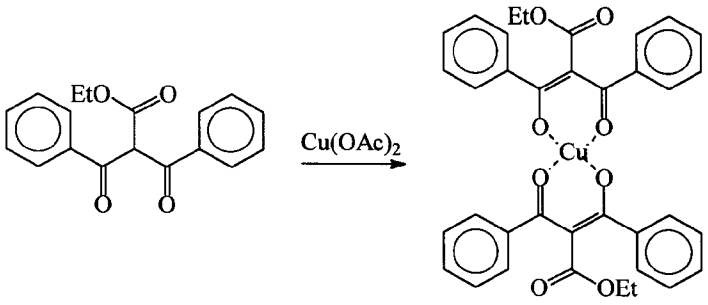
scheme 5.8

5.3 Copper complex formation

For the formation of the copper complexes, the two classes of complexes have been examined; complexation with the keto-ester moieties on both sides of the copper anion as well as the mixed complexes, with the keto-esters on one side and at the other side pentane-2,4-dione (acetylacetone). The two different strategies are outlined in sections 5.3.1 and 5.3.2 below.

5.3.1 Keto-esters on both sides

Complexation of the keto-ester moieties was achieved with copper acetate. Thus, ethyl 2-benzoyl-3-oxo-3-phenyl-propionate (**5.5**) and a half equivalent copper(II)acetate were mixed and the green crystalline precipitate collected, affording **5.14** in 74% (scheme

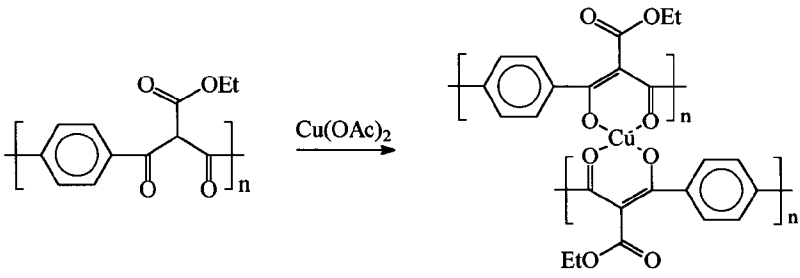


5.5 5.14

scheme 5.9

5.9). The reaction of the ethyl ester substituted polymer **5.9** with copper(II)acetate resulted in an instantaneous precipitation of a completely insoluble green solid (scheme 5.10). This insolubility, together with the fact that precipitation occurred immediately, presumably prohibited the formation of the all-complexed product **5.15**. For the copper complex of the

ethyl ester substituted polymer, insolubility is not surprisingly since the parent polymer already has a limited solubility in DMF. However, when applied to the soluble hexyl substituted polymer **5.13**, the same precipitation and insolubilty were observed.

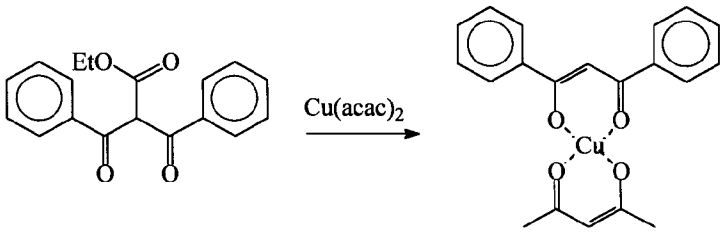


5.9 5.15

scheme 5.10

5.3.2 Mixed complexes

To prevent the cross linking of the polymer chains and to increase the concentration of copper in the material, mixed complexes were synthesized. Copper(II) acetylacetonate ($Cu(acac)_2$) was used because the boiling point of acetylacetone (133°C) made the removal of one acetylacetone equivalent from the reaction mixture possible. The reaction of ethyl 2-benzoyl-3-oxo-3-phenyl-propionate (**5.5**) with one equivalent of copper(II) acetylacetonate in boiling xylene not only afforded the ligand exchange but also resulted in the decarboxylation of the keto-ester moiety, resulting in the formation of **5.16**

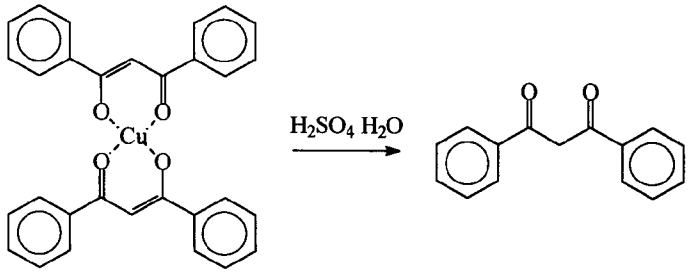


5.5 5.16

scheme 5.11

(scheme 5.11). Unambiguous proof of this phenomenon was obtained as outlined in scheme 5.12. The reaction of two equivalents **5.3** with $Cu(acac)_2$ afforded **5.17**. Hydrolysis of the complex **5.17** with dilute sulfuric acid afforded dibenzoylmethane (**5.18**). The hexyl ester derivative **5.11**, not surprisingly, readily complexated and decarboxylated as well upon reaction with $Cu(acac)_2$. Complexation of the polymers required longer reaction

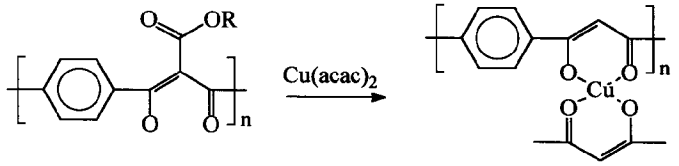
times and, especially in the case of the hexyl substituted derivative **5.13**, the use of a higher boiling solvent such as mesitylene accomplished higher conversions (scheme 5.13). The conversion could be monitored by the disappearance of the ester functionalities. A further increase in the reaction temperature by using o-dichlorobenzene caused degradation



5.17 5.18

scheme 5.12

of the materials as showed by the formation of metallic copper. During the reaction, however, the products precipitated from the reaction mixture and were isolated as green insoluble solids.



5.9 R=Ethyl
5.13 R=Hexyl

5.21

scheme 5.13

5.4 Characterization

First, a complete analysis has been performed on the keto-ester derivatives. ^{1}H-NMR of the model compounds **5.3** and **5.11** reveals the possible existence of three conformational isomers; the all-keto- and two different enol-isomers, of which the ester-enol is present to a minor extent. The isomeric ratio depends on the solvent; In chloroform, the all-keto-isomer is the only isomer present, whereas upon the addition of methanol the enol isomers are found as well. IR-spectroscopy proved to be very useful in the analysis of these compounds. The most pronounced characteristics for model compounds **5.3** and **5.11** are the presence of three distinct carbonyl vibrations; one arising

from the ester functionality at 1730 cm^{-1} and two from the ketone moieties at 1682 cm^{-1} and 1670 cm^{-1}. Oligomer **5.8** exhibits a comparable pattern, although the ketone vibrations no longer are separated (the ester- and ketone-vibrations are found at 1721 cm^{-1} and 1687 cm^{-1}, respectively). For the polymers **5.9** and **5.13**, the signals broaden, but the positions essentially are in the same range (the maxima are found at 1746 cm^{-1} and 1674 cm^{-1}). The polymers furthermore display a strong C-O vibrational band at 1250 cm^{-1}.

Upon complexation, with the keto-ester moiety on both sides of the copper complex, there is a dramatic shift of the carbonyl vibrations. For model compound **5.14** the vibration of the ester shifts from 1730 cm^{-1} to 1700 cm^{-1}, whereas the ketone absorptions disappear, and two new signals are found at 1585 cm^{-1} and 1551 cm^{-1}. One signal is due to the complexed carbonyl and the other arises from the enol double bond. Polymer **5.9**, upon complexation with copper acetate, to provide the assumed structure **5.15**, displays a decrease of the carbonyl intensities, but these have not disappeared completely.

For the mixed complexes the changes are even more dramatic since both complexation and decarboxylation occurs. Compound **5.17**, with two dibenzoyl methane moieties exhibits several absorptions; one of medium strong intensity at 1592 cm^{-1} and three strong absorptions at 1544 cm^{-1}, 1524 cm^{-1} and at 1400 cm^{-1} arising from the enol double bond, the ketone and C-O-Cu vibrations, respectively. Copper acetylacetonate on the other hand absorbs strongly at 1576 cm^{-1} and has a characteristic signal of lower intensity at 780 cm^{-1}. The mixed complex **5.16** clearly displays a combination of absorptions of both compounds. Polymer **5.19** displays the same combination as well; strong absorptions at 1576 cm^{-1} and 1521 cm^{-1} and a weaker, but significant signal at 780 cm^{-1}. Additionally, the strong ester vibration at 1250 cm^{-1} has disappeared, and the alkyl absorptions above 2900 cm^{-1}, although still present, are of low intensity. However, the copper content of this polymer is 13% whereas for a complete complexation (structure **5.19**) a copper concentration of 20% is expected.

Conductivity measurements have been carried out on a pressed pellet; due to the insolubility it was not possible to obtain free standing films. For the materials, both with the keto esters on both sides and the mixed complexes, resistance values in the order of 10^9 ohm have been found, i.e. the materials display no significant conductivities.

5.5 Discussion

The synthesis of 1,3-diketones via the acylation of β-keto esters with sodium hydride proceeds in high yields with complete C-acylation, not only for small molecules but also for oligomers. Although the use of Meldrum's acid provides an attractive route for the monomer synthesis that allows the introduction of all kinds of esters, we found that the

reaction of acid chlorides with Meldrum's acid failed for aromatic acid chlorides. Although the reaction of both aliphatic and aromatic acid chlorides with Meldrum's acid have been reported, we have found that the reaction only proceeds with aliphatic acid chlorides. However, the ethyl substituted monomer can be synthesized in good yields using monoethyl malonate. Subsequent trans-esterification readily affords the hexylester substituted monomer. Polymerization provides the polymers of which only the hexylester derivative is completely soluble. The polymer is of high purity, but contains some low molecular weight material, decreasing the average molecular weight and strongly increasing the polydispersity index.

Deprotonation and complexation are carried out in one step by the reaction with copper(II)acetate, to yield highly stable compounds. The complexation of the polymers, however, immediately results in the precipitation of the material. This precipitation is accompanied by an incomplete formation of the copper complexes; IR spectroscopy displays the presence of considerable amounts of free keto-esters. Mixed complex formation offers a good alternative to prevent this cross-linking, but is accompanied by decarboxylation that reduces the solubility since the ester functionality is the solubilizing group. Based on IR analysis, however, the mixed complexes are formed with high conversions, but the failure to incorporate the theoretical amount of copper suggests that not all the 1,3-diketone moieties are complexed. This means that the decarboxylation takes place even when the complex is not yet formed, and the insolubility as a result of the decarboxylation prevents further complex formation. The fact that both the ethyl ester and the hexyl ester derivatives produce similar complexes (based on IR spectroscopy), although their solubilities differ considerably, supports the argument that complexation is not required for decarboxylation to occur. The absence of significant conductivities in the materials is likely to be a result of this incomplete complexation, but it is also possible that the created negative charge is situated solely on the oxygens. Consequently, the mobility of the created charge carriers is too low, and no conductivity is found.

5.6 Concluding remarks

In this chapter we have described the synthesis of 1,3-diketones via a highly efficient route. The efficiency of the synthesis arises from the presence of the activating ester group. Deprotonation and complexation with a metal ion proceeds with high conversions, but when applied to polymers the insolubility prevents complete complex formation. With mixed complexes, the gain in solubility by the absence of cross-linked polymer chains is nullified by the decarboxylation of the solubilizing ester functionalities.

In both instances the copper content is too low and this together with the high charge density on the oxygen atoms results in completely insulating materials. The conductivity properties may be improved by reduction of the materials, either by the addition of a reductor, orby using other metal ions, which both reduce the polymeras well as complexate the generated anions.

5.7 Experimental part

For general remarks see sections 2.7 and 3.5

Ethyl 2-benzoyl-3-oxo-3-phenyl-propionate (5.5)

To a suspension of NaH (250 mg, 10 mmol, from 450 mg 55% in oil) in ether (20 ml) was added dropwise ethyl benzoylacetate (**5.3**) (2 g, 10 mmol) in ether (30 ml) at 0°C. The mixture was stirred at RT for an additional 15 min, and recooled to 0°C. Benzoylchloride (**5.4**) (1.47 g, 10 mmol) in ether (20 ml) was added and the mixture allowed to reach RT and stirred for 2 h. The yellow mixture was poured into cold diluted HCl, the layers separated and the aqueous phase extracted with ether (2x50 ml). The combined organic layers were washed with water, brine and dried (NaSO4). Evaporation of the solvent and crystallization from MeOH afforded 2.4 g (81%) of **5.5** as a white solid. m.p.: 109.7-110.6°C (Lit[5]: 110-112°C) IR (KBr): 1730 (s), 1682 (s), 1670 (s), 1307 (s), 1289 (s), 765 (m), 686 (m) cm^{-1}.

Malonic acid mono ethyl ester (5.2)

To a solution of diethyl malonate (150 g, 1 mol) in EtOH (600 ml) was added a solution of KOH (52.5 g, 1 mol) in EtOH (600 ml) over a period of one hour and stirred overnight. The mixture was refluxed for two hours, the clear solution cooled and the resulting solid collected and washed with ether. The crude potassium salt was dissolved in (50 ml) water and acidified with HCl (conc) at 0°C. Extraction with ether (3x150 ml), drying and evaporation of the solvent afforded 89 g (72%) of **5.4** as a colorless oil.

3-[4-(2-Ethyloxycarbonyl-acetyl)-phenyl]-3-oxo-propionic acid ethyl ester (5.7)

A solution of malonic acid monoethyl ester (**5.2**) (66 g, 0.5 mol) and 2,2'-bipyridine (15 mg) in THF (1.1 l) was cooled and n-BuLi (2.5 M, 400 ml) was added keeping the temperature below -15°C until the purple color remained for one minute. After recooling to -70°C, terephthaloylchloride (**5.5**) (25.4 g, 125 mmol) in THF (150 ml) was added and the mixture stirred for an additional hour at -50°C. The reaction mixture was allowed to warm and at -25°C it was poured into 1N HCl (750 ml) and extracted with ether (4x150 ml). The organic layers were washed with water a $NaHCO_3$ solution, brine and dried (Na_2SO_4). Evaporation of the solvents and recrystallization from ether afforded 18.2 g (48%) of **5.7** as a white solid. mp: 67.4-68.8°C. (Lit[13]: 70°C) ^{1}H-NMR ($CDCl_3$) displayed the existance of three conformations; the all-keto δ:1.25 (t, 6H); 3.95 (s, 4H); 4.19 (q, 4H); 7.98 (s, 4H) ppm, the all-enol δ: 1.15 (t, 6H); 4.11 (q, 4H) 5.64 (s, 2H); 7.70 (s,

13 Beilstein's "*Handbuch der Organischen Chemie*" **10**, II, 637

2H); 12.47 (s, 2H) ppm, and the enol-keto isomer δ: 1.15 (t, 6H); 3.94 (s, 2H); 4.11 (q, 4H) 5.66 (s, 1H); 7.67 (d, 2H); 7.91 (d, 2H); 12.46 (s, 1H) ppm.

1,4-Bis-(2-ethyloxycarbonyl-3-oxo-3-phenyl-propionyl)-benzene (5.8)

A solution of **5.7** (1 g, 3.3 mmol) in THF (10 ml) was added dropwise to a mixture of NaH (157 mg from 270 mg 60% NaH in oil, washed with hexane) in THF (10 ml) at 0°C. The yellow solution was allowed to reach RT and stirred for an additional 30 minutes, resulting in a yellow solution with a white precipitate. The mixture was cooled to 0°C and benzoylchloride (**5.4**) (920 mg, 6.7 mmol) in THF (10 ml) was added with the formation of a bright yellow solution containing a white solid. Stirring was continued for 1.5 h at RT, the mixture poured into 1N HCl (150 ml) and extracted with ether (3x150 ml). The organic layers were washed with water and extracted with a cold 10% KOH solution (2x100 ml). The yellow aqueous phase acidified and extracted with $CHCl_3$ (3x100 ml) and the organic phase washed with water, brine and dried (Na_2SO_4). Evaporation of the solvents afforded 1.5 g (80%) of **5.8** as a white solid. IR (KBr): 1721 (s), 1687 (s); 1308 (s); 1286 (s) cm^{-1}.

Poly-(2-ethyloxycarbonyl-1-(phen-1,4-diyl) propane-1,3-dione) (5.9)

A solution of **5.6** (2.0241 g, 6.6079 mmol) in THF (40 ml) was added to a emulsion of NaH (340 mg, from 620 mg 55% in oil) in THF (10 ml) over a period of 1 h at 0°C. The resulting yellow solution, containing some white solid, was stirred for an additionally 30 minutes at RT and recooled to 0°C. Terephthaloyl chloride (**5.6**) (1.3416 g; 6.6079 mmol) in THF (35 ml) was added dropwise and the bright yellow emulsion stirred overnight at RT. The mixture was poured into 10% HCl (300 ml), the solid collected and triturated with MeOH, affording 2.7 g (93%) of **5.9** as a white solid. This was stirred for three days in $CHCl_3$ (80 ml), resulting in a white suspension, and poured into MeOH (400 ml) to afford 2.2 g of **5.9**. IR (KBr): 1746 (s); 1679 (s); 1254 (vs) 856 (m) cm^{-1}.

Hexyl 3-phenyl-3-oxy-propionate (5.10)

A solution of 3-phenyl-3-oxy-propionic acid ethyl ester (**5.3**) (4.7 g, 24.5 mmol), hexanol (5 g, 49 mmol) and p-TsOH (200 mg) in toluene (100 ml) was refluxed for 70 h. Toluene was evaporated and a $NaHCO_3$ solution and ether were added. The layers were separated and the aqueous phase extracted with ether (2x50 ml). The combined organic phases were washed with brine and dried (Na_2SO_4). The solvent was removed and the residue distilled (kugelrohr, 180°C, 0.5 mm Hg) affording 4.6 g (72%) of **5.10**.

Hexyl 2-benzoyl-3-oxo-3-phenyl-propionate (5.11)

A solution of **5.10** (3 g, 11.5 mmol) in ether (20 ml) was added dropwise to a suspension of NaH (275 mg) in ether (10 ml) at 0°C in 30 min, and the mixture stirred at RT for an additional 15 min. After recooling to 0°C benzoylchloride (**5.4**) (1.62 g, 11.5 mmol) in ether (30 ml) was added and the mixture allowed to reach RT and stirred for 2 h. The yellow mixture was poured into cold diluted HCl, the layers separated and the aqueous phase extracted with ether (2x50 ml). The combined organic layers were washed with water, brine

and dried (Na_2SO_4). Evaporation and crystallization from hexane afforded 2.5 g (62%) of **5.11** as a white solid. mp: 70.3-71.8°C. ^{1}H-NMR ($CDCl_3$) δ: 0.83 (t, 3H), 1.19 (m, 6H), 1.57 (m, 2H), 4.21 (t, 2H), 6.20 (s, 1H), 7.47 (m, 4H), 7.57 (m, 2H), 7.92 (m, 4H) ppm. Anal. calcd. for $C_{22}H_{24}O_4$: C 74.98, H 6.86, found: C 75.18, H 6.97. HRMS calcd. for $C_{22}H_{24}O_4$: 352.167, found: 352.166.

3-[4-(2-Hexyloxycarbonyl-acetyl)-phenyl]-3-oxo-propionic acid hexyl ester (5.12)

A mixture of diester **5.7** (4.35 g, 14.2 mmol), hexanol (3.2 g, 30 mmol) and p-TosOH (50 mg) in toluene (200 ml) was refluxed overnight. The toluene was evaporated and to the residue was added a $NaHCO_3$ solution (100 ml). Extraction with ether, drying (Na_2SO_4) and evaporation afforded a solidifying oil. Recrystallization from hexane gave 4.35 g (74%) of **5.12** as a white solid. mp: 59.4-60.7°C. Anal. calcd. for $C_{24}H_{34}O_6$: C 68.88, H 8.19, found: C 68.79, H 8.32.

Poly-(2-hexyloxycarbonyl-1-(phen-1,4-diyl) propane-1,3-dione) (5.13)

To a mixture of NaH (400 mg, 10 mmol) in THF (10 ml) was added dropwise a solution of **5.12** (1.6802 g, 4.0145 mmol) in THF (25 ml) over a period of 20 min at a tempreature of 10°C and stirred at RT for another 30 min. To the resulting yellow solution was added a solution of terephthaloyochloride (**5.6**) (815 mg) in THF (35 ml) in 30 min at 10°C. The yellow solution was left overnight at RT and poured into water (250 ml) containing HCl (15 ml, conc). The aqueous phase was decanted, the resulting white semi-solid dissolved in chloroform and dried (Na_2SO_4). The volume was reduced to 7 ml and the product precipitated in hexane affording 1.75 g (80%) of **5.13** as a white solid. IR (KBr): 2957 (s), 2930 (s), 1746 (m), 1674 (s), 1590 (s), 1253 (vs), 859 (m) cm^{-1}. Anal. calcd. for $(C_{16}H_{18}O_4)_n$: C 70.06, H 6.61, found: C 69.45, H 6.62.

Ethyl 2-benzoyl-3-oxo-3-phenyl-propionate copper(II)-complex (5.14)

A solution of **5.5** (270 mg, 0.9 mmol) in warm EtOH (30 ml) was added to a solution of $Cu(OAc)_2.H_2O$ (90 mg, 0.45 mmol) in 20 ml water-EtOH 1:1 and stirred for 30 minutes. The resulting green solid was collected yielding 220 mg (75%) of **5.14**. mp: 219.2-221.5°C. IR (KBr): 1700 (m); 1585 (s); 1551 (s); 1395 (s); 1104 (s); 695 (m) cm^{-1}.

1,3-Diphenyl propane-1,3-dione-acetylacetone copper(II) complex (5.16)

A mixture of hexyl 2-benzoyl-3-oxo-3-phenyl-propionate (**5.12**) (195 mg, 0.7 mmol), $Cu(acac)_2$ (172 mg, 0.7 mmol) in xylene (15 ml) was refluxed for 2 h. The mixture was cooled to RT and hexane (15 ml) was added to afford 167 mg (65%) of **5.16** as a green-gray solid. IR (KBr): 1577(s); 1541 (s); 1521 (s); 1399 (s); 781 (m); 745 (m) cm^{-1}.

1,3-Diphenyl propane-1,3-dione copper(II) complex (5.17)

A mixture of hexyl 2-benzoyl-3-oxo-3-phenyl-propionate (**5.11**) (712 mg, 2 mmol) and $Cu(acac)_2$ (216 mg, 1 mmol) in xylene (30 ml) was refluxed for 2 h. The reaction mixture was cooled to -25°C and the green solid collected. Recrystallization from xylene afforded 358 mg (70%) of **5.17** as a green solid. mp: 300°C (d). IR

(KBr): 1592 (m), 1544 (s), 1524 (s), 1400 (s), 744 (m) cm^{-1}. Anal. calcd. for $C_{30}H_{22}O_4Cu$: C 70.65, H 4.35, Cu 12.46 found: C 70.05, H 4.46, Cu 12.37.

1,3-Diphenyl propane-1,3-dione (5.18)

A mixture of copper complex **5.17** (135 mg, 0.26 mmol), 25% H_2SO_4 (10 ml) and ether (10 ml) was stirred for 1.5 h untill the initial green color had dissapeared. The layers were separated and the aqueous phase was extracted with ether. The combined organic layers were washed with water a $NaHCO_3$ solution , brine and dried (Na_2SO_4). Evaporation of the solvent and recrystallization from hexane afforded 40 mg (68%) of **5.18** as white needles. mp: 74-75°C (lit[14] 77-78°C).

Polymer copper complex 5.19

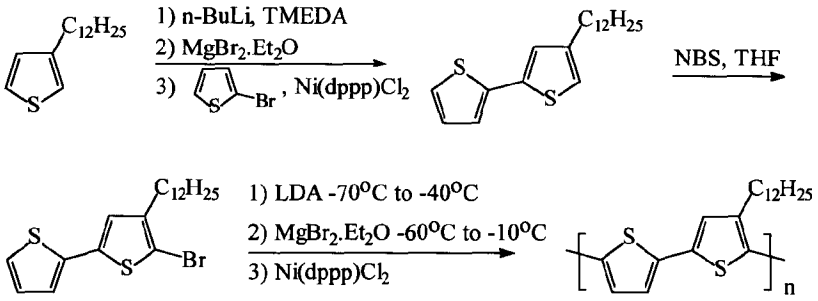
A solution of **5.13** (353 mg, 1.29 meq) and $Cu(acac)_2$ (337 mg) in mesitylene (30 ml) was refluxed overnight. The mixture was cooled and the resulting solid collected, washed with chloroform, ether and dried. This afforded 410 mg of **5.21** as a green solid. IR (KBr): 1576 (s); 1521 (s); 1418 (s); 1383 (s); 780 (m) cm^{-1}. Anal. calc. for $(C_{14}H_{12}O_4Cu)_n$: C 54.63, H 3.93, Cu 20.64; found C 56.22, H 4.01, Cu 13.92.

14 Beilstein's "*Handbuch der Organischen Chemie*" 7, IV, 2512

Samenvatting

De ontwikkeling van π-geconjugeerde polymeren heeft de laatste 15 jaar een hoge vlucht genomen. Deze belangstelling is afkomstig uit de wetenschappelijke wereld, maar ook, en in toenemende mate, vanuit de industriële laboratoria. De belangrijkste reden voor deze ontwikkeling is het feit dat de geconjugeerde materialen een groot aantal interessante optische en niet lineair optische eigenschappen vertonen. Bovendien kunnen ze na oxidatie of reductie stroom geleiden. Een groot aantal toepassingen zijn als gevolg van deze eigenschappen mogelijk, en een gedeelte wordt al min of meer commercieel gebruikt. Een bekende eigenschap van geconjugeerde polymeren is de lage oplosbaarheid. Deze lage oplosbaarheid heeft in het verleden de ontwikkeling ernstig belemmerd, doordat de materialen hierdoor zowel slecht te karakteriseren als te verwerken zijn. Veel onderzoek heeft geleid tot een tweetal oplossingen voor dit probleem. De eerste is het gebruik van een pre-polymeer, dat nog niet geconjugeerd is en mede daarom oplosbaar. Na verwerking en karakterisering wordt het pre-polymeer, meestal door verhitting, omgezet in het onoplosbare geconjugeerde systeem. Het alternatief is het gebruik van gesubstitueerde polymeren; lange, voornamelijk alkyl groepen die zich aan de zijkant van de starre geconjugeerde polymeerketen bevinden, verhogen de oplosbaarheid van het gehele polymeer. Op beide methodes is een grote variatie van synthesen gebaseerd. Een overzicht hiervan is gegeven in het eerste hoofdstuk.

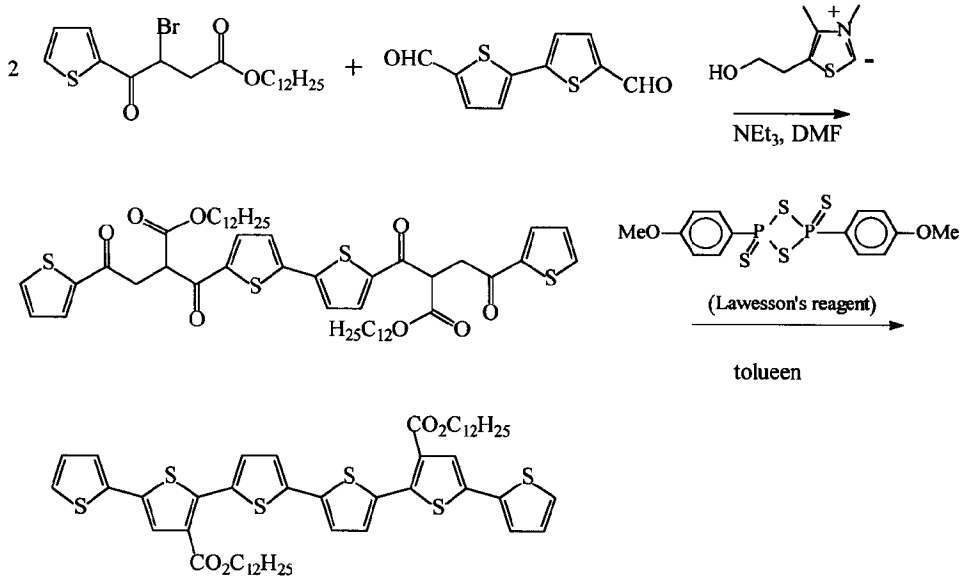
Een belangrijk aspect van de geconjugeerde materialen is de effectieve conjugatie lengte daar deze voor het grootste gedeelte de eigenschappen van de materialen bepaalt. De substituenten, hoewel deze de oplosbaarheid verhogen, hebben een negatieve invloed op de effectieve conjugatie. Dit komt door de ruimtelijke invloed van de substituenten op de ringen, en eventueel op elkaar, waardoor de aromatische ringen uit het vlak draaien en zo een gedeelte van de conjugatie verliezen. Zowel de posities van de substituenten ten opzichte van elkaar als het relatieve aantal substituenten hebben hierop invloed. In hoofdstuk twee is de synthese beschreven van een polythiofeen, waarbij de substituenten allemaal dezelfde kant opstaan (de zogenaamde head-to-tail koppeling) en er één substituent per twee thiopheen ringen is. De synthese is gebaseerd op het werk van de groep van McCullough, waarbij een selectief gemaakt mono-Grignard mono-bromide met behulp van een nikkel-katalysator wordt gepolymeriseerd. In dit geval hebben we gebruik gemaakt van een mono gesubstitueerd bithienyl derivaat met een selectief ingevoerd broomatoom. De selectiviteit is ontleend aan de invloed van de substituent in de bromeringsreactie. In schema 1 is de synthese van zowel het monomeer als het polymeer weergegeven. Verder is in het tweede hoofdstuk de synthese van een vergelijkbaar polymeer beschreven met dit verschil dat de substituenten niet het regelmatige patroon vertonen, en zijn de absorptie



schema 1

eigenschappen van de twee polymeren met elkaar vergeleken. Beide polymeren vertonen thermochrome karakteristieken. Van het regelmatig gesubstitueerde polymeer is het effect veel sterker; de kleur verschuift van paars bij kamertemperatuur tot oranje bij 100 graden. Het opvallendst is dat de reversibiliteit, dat bij andere gesubstitueerde polythiophenen zeer snel is, in het geval van het regelmatig gesubstitueerde polymer langzaam is. Het duurt drie dagen voordat na afkoelen de paarse kleur weer terug komt. Dit verschijnsel is een gevolg van de regelmatigheid van de substituenten. Deze regelmatigheid zorgt ervoor dat de substituenten niet alleen dezelfde kant op wijzen, maar bovendien allemaal aan dezelfde kant van de uit thiofeen ringen bestaande hoofdketen liggen.

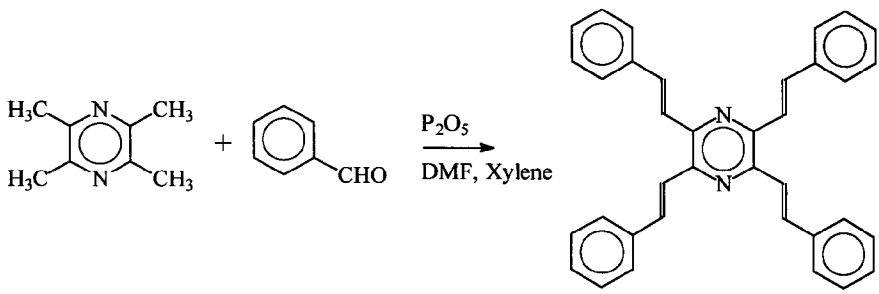
De hierboven beschreven organometaal koppeling, waarvan nog vele varianten bekend zijn, is een veel gebruikte methode voor de synthese van poly- en oligoaromaten. Een andere methode voor de synthese van bijvoorbeeld thiopheen oligomeren is de ringsluiting van diacetylenen en 1,4-diketonen. In het derde hoofdstuk wordt deze benadering gebruikt voor de bereiding van oligomeren bestaande uit verschillende aromatische ringen en voorzien van diverse soorten substituenten. De basis vormt de Stetter reactie, waarbij een cyanohydrin derivaat van een aromatisch aldehyde addeert aan een α-β onverzadigd keton of een gemaskeerde vorm hiervan. Zowel het cyanide anion als een van een thiazolium zout afgeleid ylide kunnen worden gebruikt als katalysator voor de vorming van het cyanohydrin. Het hierbij verkregen 1,4-diketon wordt vervolgens ringgesloten met Lawesson's reagens tot het overeenkomstige thiopheen, of met ammonium acetaat wat het pyrrool geeft. Een voorbeeld van deze methode is weergegeven in schema 2. In dit geval wordt een bromide gebruikt als gemaskeerd α-β onverzadigd keton, dat door de reactie met triethylamine wordt gegenereerd. De reactie met het dialdehyde en de ringsluiting van het ontstane tetraketon geeft het thiopheen oligomeer. In tegenstelling tot alkyl substituenten veroorzaken de twee ester groepen geen verlaging van de effectieve conjugatie, doordat ze loodrecht op de thiopheen ringen staan waardoor de ringen in conjugatie met elkaar blijven. De combinatie van de Stetter reactie met de ringsluiting van de diketonen is verder



schema 2

ook nog gebruikt voor de synthese van polymeren. Hoewel de poly-1,4-diketonen niet volledig aromatisch zijn is de oplosbaarheid klein, wat als consequentie heeft dat de verkregen materialen lastig te zuiveren en te karakteriseren zijn. Het invoeren van substituenten in de monomeren is goed uitvoerbaar, maar de reactiviteit van het gemaskeerde onverzadigde keton neemt door de substituenten zoveel toe dat er ook ongewenste nevenreacties optreden.

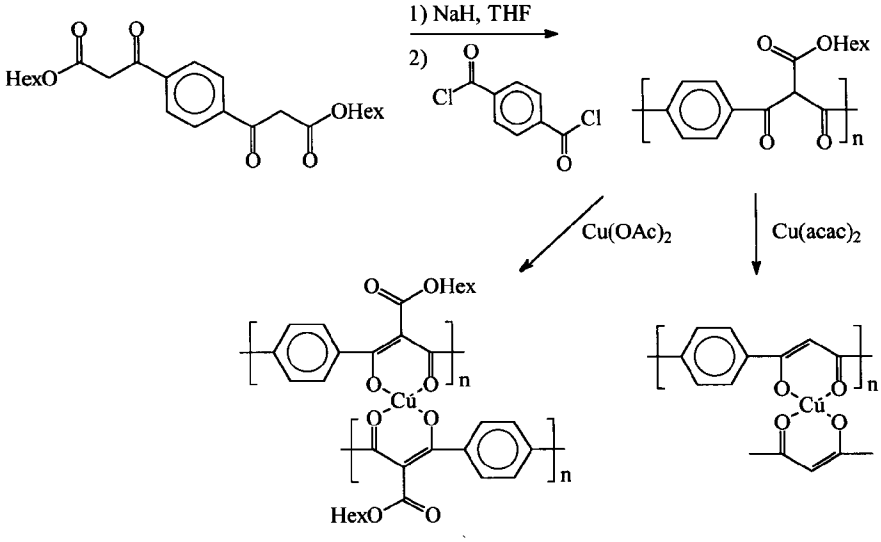
Behalve de in hoofdstuk twee en drie beschreven manieren om via een beperkt aantal substituenten, door de substituenten selectief in te voeren en door sterisch kleine



schema 3

groepen te gebruiken is er nog een manier om een hoge effectieve conjugatie lengte te verkrijgen. Deze methode is beschreven in hoofdstuk vier en omhelst de synthese van twee-dimensionale systemen. Hierbij wordt uitgegaan van de pyrazine eenheid als centraal vertakkingspunt. Door middel van de zuur gekatalyseerde condensatie van methylpyrazines met aromatische aldehydes worden de gewenste moleculen verkregen. Een voorbeeld is gegeven in schema 3. De dubbele band tussen de aromatische ringen is essentieel om de vlakke structuur te verkrijgen. Van verbinding 54 is de ruimtelijke structuur bepaald door middel van een röntgenanalyse. Dit heeft onomstotelijk de vlakheid van het systeem aangetoond. Vergelijking van de UV-waarden van de twee-dimensionale structuren met de één-dimensionale equivalenten heeft duidelijk de verhoging van de effectieve conjugatie lengte aangetoond.

De meeste geconjugeerde polymeren worden pas geleidend na oxidatie of reductie. Verreweg het meeste onderzoek is gericht op de geoxideerde systemen (p-type doping), omdat deze zowel het makkelijkst te maken als het stabielst zijn. Behalve door oxidatie of reductie zijn er ook voorbeelden van geleidende polymeren door het protoneren of deprotoneren van de isolerende vorm. Dit leidt tot p- respectivelijk n-type gedoopte geleidende polymeren, waarbij de stabiliteit van de gedeprotoneerde vorm te wensen overlaat. In hoodstuk vijf wordt de synthese van een 1,3-diketon polymeer beschreven. Deprotonering van dit polymeer en de complexatie van de gegenereerde anionen met koperionen zou een stabiel n-type gedoopt geleidend polymeer moeten geven. De synthese van het 1,3-diketon polymeer is weergegeven in schema 4. Voor de complexatie zijn twee benaderingen



schema 4

onderzocht. De eerste gaat uit van een koperion dat aan twee kanten is omringd door het polymeer, waarbij de oplosbaarheid drastisch achteruit gaat. In de tweede benadering is het koperion omringd door het polymeer aan een kant en een ander, kleiner ligand aan de andere kant. Dit om de oplosbaarheid van het systeem te verhogen. Door de zijreactie van de ester functionaliteit is dit echter zeer beperkt. Hoewel het geleidingsvermogen van de hier beschreven poly-1,3-diketonen nog erg laag is, is hiermee wel een eerste aanzet gegeven voor de synthese van stabiele n-type gedoopte geleidende materialen.